

C. V. RAMAN

1888 CENTENNIAL 1988



1888-1970



Journal of the

INDIAN INSTITUTE OF SCIENCE

Vol. 68, Nos 11-12, Nov.-Dec., 1988

Editorial Committee

Editor:

M. Vijayan

Associate Editor:

R. Narayana Iyengar

Executive Editor:

P. R. Mahapatra

Technical Officer (Editorial):

K. Sreenivasa Rao

Members

Anil Kumar

R. K. Kaul

S. S. Krishnamurthy

B. G. Raghavendra

M. R. S. Rao

A. P. Shivaprasad

J. Srinivasan

N. Viswanadham

R. Vittal Rao

Guest Editors:

N. Mukunda

T. V. Ramakrishnan

D. P. Sen Gupta

Enquiries to:

The Executive Editor,

Journal of the Indian Institute of Science,

C/O IISc Library, Bangalore 560 012, India.

ISSN No. 0019-4964

**This
publication
is available in
microform
from University
Microfilms
International.**



Call toll-free 800-521-3044. Or mail inquiry to:
University Microfilms International, 300 North
Zeeb Road, Ann Arbor, MI 48106.

Cover design: D. P. Sen Gupta and N. Mukunda

Special Issue

**CHANDRASEKHARA VENKATA RAMAN
CENTENARY**

Chandrasekhara Venkata Raman
November 7, 1897 - November 7, 1970



Courtesy: T. M. K. Nedungadi

Chandrasekhara Venkata Raman
November 7, 1888–November 21, 1970

FOREWORD

Last year was the birth centenary of the mathematical genius Srinivasa Ramanujan. This year we celebrate the centenary of the scientific colossus Chandrasekhara Venkata Raman.

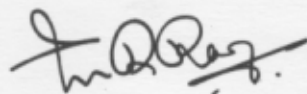
Raman is the greatest physicist and experimental scientist this country has so far produced. He was totally self-made and self-taught, his only true "teachers" being Rayleigh and Helmholtz through their writings. In some ways he may be viewed as the last in their line of classicists, though his own work, in the words of R. W. Wood, gave "one of the most convincing proofs of the quantum theory of light". Raman was blessed with supreme self-confidence, boundless curiosity to understand Nature, infinite sensitivity to her nuances, and a deep sense of patriotism. In addition to these remarkable qualities, he was able to inspire those around him to achievements of an order they could not have reached on their own.

With indefatigable energy and a "European intensity" no other Indian scientist exhibited, in the period 1907 to 1933 Raman created and sustained a school of physics in Calcutta that in Sommerfeld's words made this country "an equal partner with her European and American sisters". Even before the discovery of the Raman Effect in 1928 which led to the award of the Nobel Prize in 1930, Raman had done outstanding work in acoustics and light scattering recognised by his election to Fellowship of the Royal Society in 1924.

We at this Institute remember Raman as our first Indian Director from 1933 to 1937, and thereafter as Professor and Head of the Department of Physics (set up by him in 1933) until his retirement in 1948. Here too he created an outstanding school of physics with memorable contributions such as the Raman-Nath theory of diffraction of light by ultrasonic waves and the Raman-Nedungadi discovery of the "soft mode", among others. It was also in the Bangalore period, in 1934, that Raman established the Indian Academy of Sciences.

In our one-day symposium arranged to pay tribute to Raman, we have invited a group of distinguished scientists to speak to us of Raman's life and work, the contributions of his school in Bangalore, and the present scope and applications of the Raman Effect. This special issue of the *Journal of the Indian Institute of Science* brought out on this occasion contains the texts of these talks, some rare photographs, and reprints of some of Raman's most significant papers.

On Raman's birth centenary it is appropriate that we remind ourselves of the great qualities that he possessed, and the ideals and dreams of self-reliance and independence that he cherished.



C. N. R. RAO
Director

Bangalore
November 1988

Indian Institute of Science

Chandrasekhara Venkata Raman Centenary 1988

A Special issue of the
Journal of the Indian Institute of Science

CONTENTS

M. A. Viswamitra	Professor C. V. Raman and the Department of Physics, Indian Institute of Science, 1933-1948	445
G. Venkataraman	Some reflections on the life and science of Sir C. V. Raman	449
A. K. Sood	Light scattering from condensed matter—Contributions of the Raman school	461
Sudhanshu S. Jha	Some recent trends in Raman spectroscopy	483
Herbert L. Strauss	The resonance Raman spectrum of I_2 in solution	493
A. K. Ramadas	Inelastic light scattering in crystals	505
T. V. Ramakrishnan	Selected papers of Raman: An introduction	509
	Selected papers of Raman	
	(i) Contents	517
	(ii) Reprinted papers	519

Professor C. V. Raman and the Department of Physics, IISc, 1933-1948

M. A. VISWAMITRA

Chairman, Department of Physics, Indian Institute of Science, Bangalore 560 012.

Professor Raman joined the IISc as Director on 31st March 1933. The Department of Physics was inaugurated in July 1933 with Prof. C. V. Raman as the first head of the Department and with eight students; namely, R. S. Krishnan, S. Jagannathan, R. Ananthakrishnan, G. Narasimhaiah, D. S. Subbaramaiah, N. S. Nagendra Nath, P. S. Srinivasan and P. Pattabhiramaiah. Later in the year, B. V. R. Rao and C. S. Venkateswaran joined.

Research was initiated in the following subjects: Doppler Effect in light scattering, colloid optics, diffraction of light by ultrasonic waves, and Raman spectroscopy. This was followed in subsequent years by crystal physics, dynamics of crystal lattices, *e.g.*, the soft mode, physics of diamond, second-order Raman spectra of crystals, X-ray topography, and Brillouin scattering.

The total number of research scholars during the period 1933-1948 was 98. Among them in addition to those already mentioned, are: K. Venkatachala Iyengar, P. Nilakantan, B. V. Thosar, S. Ramaswamy, T. M. K. Nedungadi, B. D. Saxena, Vikram A. Sarabhai, Anna Mani, P. Raman Pisharoty, G. N. Ramachandran, D. D. Pant, S. Ramaseshan, K. G. Ramanathan, V. Chandrasekharan, T. Radhakrishnan and P. S. Narayanan.

Several distinguished scientists spent considerable periods of time here. In particular, Prof. Max Born spent six months as a Visiting Professor in the Department in 1936. Dr. H. J. Bhabha joined the Department as a special Reader in Theoretical Physics, to deliver 25 lectures, in 1940. In 1942, he became a special Reader with the status of a Professor as a personal distinction, and was at the IISc till 1945.

Raman stressed in his students, the desire for excellence in research as a prime requirement and also encouraged them to develop a strong initiative for independent research. His presence and the intellectual environment he provided, brought out their best and resulted in some significant contributions from the laboratory during his tenure here. Some of these are the following:

1. The reciprocity theorem in colloid optics - R. S. Krishnan
Proc. Indian Acad. Sci., 1935, **1**, 782.

2. The diffraction of light by high frequency sound waves. Parts I, II, III, IV and V. - C. V. Raman and N. S. Nagendra Nath
Proc. Indian Acad. Sci., 1935, **A2**, 406, 413; 1936, **A3**, 75, 119, 459.
3. A new technique of complementary filters for photographing the Raman spectra of crystal powders - R. Ananthakrishnan
Curr. Sci., 1936, **5**, 131.
4. Light scattering and fluid viscosity - C. V. Raman and B. V. Raghavendra Rao
Nature, 1938, **141**, 242.
5. Effect of temperature on the Raman spectrum of quartz - T. M. K. Nedungadi
Proc. Indian Acad. Sci., 1940, **A11**, 86.
6. Raman Effect and crystal symmetry - B. D. Saxena
Proc. Indian Acad. Sci., 1940, **A11**, 229.
7. The α - β transformation of quartz - C. V. Raman and T. M. K. Nedungadi
Nature, 1940, **145**, 147.
8. Interferometric studies of light scattering - C. S. Venkateswaran
Proc. Indian Acad. Sci., 1942, **A15**, 316, 322, 362, 371.
9. New concepts of the solid state - C. V. Raman
Curr. Sci., 1942, **11**, 85.
10. The physics of diamond - C. V. Raman
Curr. Sci., 1942, **11**, 261.
11. The Raman spectrum of diamond - R. S. Krishnan
Proc. Indian Acad. Sci., 1944, **A19**, 216.
12. X-ray topographs of diamond - G. N. Ramachandran
Proc. Indian Acad. Sci., 1944, **A19**, 280.
13. The photoconductivity of diamond - D. D. Pant
Proc. Indian Acad. Sci., 1944, **A19**, 315, 325.
14. The crystalline forms of the Panna diamonds - S. Ramaseshan
Proc. Indian Acad. Sci., 1944, **A19**, 334.
15. Raman spectra of second order in crystals: calcite gypsum, quartz - R. S. Krishnan
Proc. Indian Acad. Sci., 1945, **A22**, 182, 274, 329.
16. The Faraday Effect in diamond - S. Ramaseshan
Proc. Indian Acad. Sci., 1946, **A24**, 104.
17. Infrared spectrum of diamond - K. G. Ramanathan
Nature, 1945, **156**, 23.
18. A Theory of the crystal forms of diamond - S. Ramaseshan
Proc. Indian Acad. Sci., 1946, **A24**, 122.
19. The phosphorescence of diamond - V. Chandrasekharan
Proc. Indian Acad. Sci., 1946, **A24**, 193.
20. A home made infrared spectrometer - K. G. Ramanathan
Curr. Sci., 1946, **15**, 184.
21. The vibration spectra of the alkali halides - R. S. Krishnan and P. S. Narayanan
Proc. Indian Acad. Sci., 1949, **A28**, 296.
22. The influence of optical activity on light scattering in quartz - V. Chandrasekharan
Proc. Indian Acad. Sci., 1949, **A28**, 409.

23. The Raman spectrum of ammonium dihydrogen phosphate – P. S. Narayanan
Proc. Indian Acad. Sci., 1949, **A28**, 469.

Many of these are superb contributions and measure up to the best published anywhere at that time in the areas of optics and crystals. The list given also tells us how Raman not only inspired his students to take up forefront research problems but also encouraged them to publish the results by themselves.

Opening new lines of experimental physics research goes much beyond manipulation of available equipment. Raman stressed the determining role played by our ability to create our own instruments and newer techniques. He created departmental workshops in addition to the central workshop and produced some excellent results with a home-made spectrometer and a three-metre spectrograph. No less was Raman's emphasis on developing experiments in close interaction with theory.

After Prof. Raman's retirement, the main course of research in our Department continued on the lines set by him, for several years. But the decades that have now followed naturally have brought about many changes, with some research activities withdrawn and some recast and strengthened. Our major efforts are in condensed-matter physics, experimental as well as theoretical. We have also taken up some newer areas like the physics of biomolecular systems. Many of the boundaries between conventional sciences disappear when biological systems are studied to their end. To the physicists concerned with understanding the way nature works, biology offers a unique scope and some most fascinating and challenging problems. Raman himself in his later years took up some of these studies and was deeply concerned with questions related to vision and colour. Everything that involved light fascinated the great scientist. Our own studies on DNA, I hope, will one day lead to exploring problems involving the effect of light; like how the genes function under light.

It is with pride and pleasure that the Department of Physics remembers its founder in the centenary year of his birth.

My own contact with Prof. Raman was years after he retired from the Department. There were a few occasions when I was fortunate to meet and talk to him in person. They were great moments. I also like to recall here his lectures at the Raman Research Institute which we used to attend, when we were students of the Department. It was not just that Raman narrated brilliantly. He assumed no prior knowledge and yet we came out with the feeling that we understood everything he said, very clearly. When Raman spoke there never was any communication gap. We are far away from those days but Raman's achievements continue to inspire our progress as in the past.

Some reflections on the life and science of Sir C. V. Raman

G. VENKATARAMAN

ANURAG, RCI Campus, Mamidipally P.O., Hyderabad 500 005, India.

Received on September 13, 1988.

It is a privilege to speak about Raman, especially in this Institute where he spent a crucial period of his life. This being the year of his birth centenary, the essential details of his life are now better known than before. In view of that and the fact that on an earlier occasion Prof. Ramaseshan has delivered a memorable lecture on Raman here in this very hall, I shall not discuss Raman's life in the usual sense of the word. Instead, I shall concentrate on some of the lesser-known aspects, in particular those associated with the period he spent here. Nevertheless, the requirement of completeness demands that I provide at least a rapid thumb-nail sketch of Raman's life, which I shall now proceed to do.

Raman was born near Tiruchirapally on November 7, 1888. At the age of four, Raman's father moved to Visakhapatnam to serve in a college there. Thus the early childhood of Raman was spent in what is now a part of Andhra Pradesh and not surprisingly Raman could speak Telugu fluently, a fact that is hardly known. Being an unusually gifted student, Raman raced through school and college and, at eighteen, emerged not only with an M.A. degree topped by several prizes, but also with a passion for physics. But in those days, a career in science for Indians was unthinkable and Raman did what was expected of him namely, enter government service as an administrator. That was in the year 1907.

The government job took Raman to Calcutta which was then the capital of India. There, working in his spare time, Raman studied many problems in physics, particularly in the area of acoustics and optics. The pursuit of science was made somewhat easy for him by the facilities provided by the Indian Association for the Cultivation of Science. It is a matter of history that though the Association was founded on the model of the Royal Institution in London, it did not function in that style, at least during the life time of its founder. The Association sprang to life only after Raman joined it and took charge.

A major turning point came when, in 1917, Raman resigned from the government service to accept the Palit Chair for Physics in the University of Calcutta, an act which was hailed by all lovers of science, particularly by Sir Asutosh Mukherjee who publicly

applauded the sacrifice Raman had made in giving up a highly lucrative career in government. The second decade of Raman's stay in Calcutta was truly a glorious period. No longer had he to work alone in the Association for he now had a big gathering of highly talented students drawn from all over the country. In fact the reputation of the Association spread even overseas, so much so the great Arnold Sommerfeld once remarked that

India had suddenly emerged in competitive research as an equal partner with her European and American sisters.

The high point of this period was undoubtedly the discovery of the Raman Effect, which brought fame and glory both to the discoverer as well as the institution he worked in.

Success also breeds envy and Raman's success was no exception. As a result of several painful incidents, Raman had to leave the Association. Fortunately for him, precisely at this time there was an invitation to become the Director of the Institute of Science. When Raman left Calcutta, it was said by the noted geologist Sir L. L. Fermor:

Calcutta's loss will be Bangalore's gain. At present Calcutta may be regarded as a centre of scientific research in India but with the transference to Bangalore of one of our leading investigators, she will have to guard her laurels.

Bangalore was no bed of roses as I shall shortly describe in detail. Nevertheless, Raman made many important contributions both as a scientist and as a leader. Unfortunately these are hardly remembered because the controversies that he was involved in eclipsed his accomplishments. In 1948 Raman retired and adjourned to the Institute he himself had founded, viz., the Raman Research Institute where he spent the remaining years of his life. This last phase was also rather a sad one, and will receive some attention later in this lecture.

I now go back to the early thirties, that is the period just before Raman took charge as the Director of this Institute. At that time he was a member of the Institute Council, having been nominated as a representative of the Eastern Group of Universities. Twice during this period he was warmly felicitated by the Council, once when the Knighthood was conferred upon him, and later when he won the Nobel Prize. Sir Martin Forster was the Director then, and his term was coming to a close on April 1, 1933. In anticipation of that, the Council appointed in July 1931, two committees which would submit names of suitable candidates for a successor. The committee in England was convened and chaired by Sir William Bragg and had Sir William Pope and Sir Robert Robertson as the other two members. The Indian committee consisted of Sir Samuel Christopher, Sir T. Vijayaraghavachariar and Sir M. Visweswarayya, the last mentioned being the Chairman and the Convenor. Both the committees unanimously favoured Raman for the post, and in July 1932 the Council recommended to the Viceroy that Raman be appointed the Director.

There was trouble right from the beginning when Sir P. C. Ray and Meghnad Saha opposed some appointments proposed by Raman. Although the opposition was notio-

nally on technical grounds, historically speaking one sees an extension of the animosity that sprang up during Raman's Calcutta period.

Upon assuming office in April, 1933 Raman did three things, namely, bring a new Physics Department into existence, restructure some of the existing departments, and finally reorganise the workshop. According to Raman, all these were for the better of the Institute but unfortunately for him, every one of these actions boomeranged.

To organise a new department, one needs money, staff and students. Raman had no problem in attracting students but he did have difficulties in finding money and in making staff appointments. The seed money he had been given was woefully inadequate to meet salaries, studentships, cost of journals, books, equipment, etc. Raman therefore reapportioned some of the Institute budget to aid the fledgeling Physics Department, an act which later invited charges of embezzlement!

Raman was firmly wedded to the view that excellent work comes from excellent people. He was quite dissatisfied with the performance of the existing departments, and strongly felt that the Institute needed fresh blood. Luckily, an opportunity for inducting new talent was presenting itself, since many eminent scientists were fleeing Hitler's Germany just then. Why not bring some of them over to the Institute? As we shall soon see, one particular appointment which he pursued with enthusiasm created a huge problem.

The reorganisation previously referred to antagonised both the Professor of Chemistry as well as the Professor of Electrical Engineering. Raman found that the Physical Chemistry Section was engaged mainly in studies relating to magnetism. Back at the Association, magnetism was one of the strong points of his research group. Feeling that the Physical Chemistry Section was somewhat isolated in relation to the other activities of the Chemistry Department, Raman decided to strengthen it by making it a part of the new Physics Department, especially since the merger would provide the chemists concerned with opportunities for constant and profitable interaction with other colleagues having allied interests. Prof. Watson, under whose care the Physical Chemistry Section had functioned earlier, was deeply offended and he resigned. Likewise, Prof. Mowdawala of the Electrical Technology Department opposed Raman's idea that the Institute Workshop, instead of merely training students, also assist research workers by building equipment for them. Mowdawala also became resentful and chose to leave. The sleepy campus was coming alive with controversy, and pretty soon it would be time for the Council to sit up and take notice, which is exactly what the opposition wanted.

The Born episode brought things to a boil. Like many others, Max Born left Germany in the early thirties and found for himself a temporary berth in Cambridge. At that time he received a letter from Raman asking for the names of bright theoretical physicists wanting to leave Germany and who could be considered for appointment at the Institute. Born replied that he could not recommend names without knowing about the conditions in India. Raman understood Born's position; so why could not Born come to Bangalore for a while and see things for himself? The Institute Council approved a temporary Readership for Max Born (as it also did for Prof. Hevesey). Born accepted the offer,

especially as his Cambridge appointment was drawing to a close. Further, Rutherford advised him to try out Bangalore as the salary was better!

In the autumn of 1935 Born and his wife Hedi sailed for India. Soon after they arrived in Bangalore, a professor of Electrical Engineering named Aston came from England. He was Mowdawala's replacement. The Astons stayed with the Borns till their own bungalow was ready. Later, Aston actively worked against Raman and also attacked Max Born.

Raman developed a great liking for Born, despite the difference of opinion he had concerning theories of lattice dynamics. He was very keen that Born should continue in the Institute as a permanent member but first he had to persuade the Faculty to accept the idea. Accordingly he proposed to the Senate that it recommend the appointment of Max Born as the Professor of Mathematical Physics. In his speech supporting the motion, Raman strongly eulogised Born but nevertheless the motion was not received well by many. As Born describes,

Aston went up and spoke in a most unpleasant way against Raman's motion, declaring that a second-rank foreigner, driven out of his country, was not good enough for them. This was particularly disappointing as we had been kind to the Astons. I was so shaken that when I returned to Hedi I simply cried.

Meanwhile the turmoil on the campus continued to grow, and in July 1935 the Council recommended to the Viceroy that a Review Committee be appointed. Unlike in the past, the Council this time spelt out in detail the various items the proposed Committee should address itself to. The list was heavily loaded against Raman and his protests were over-ruled.

Unmindful of all this, Raman continued to steadfastly campaign for Born's appointment and in fact in November 1935 the Council even accepted his suggestion that a professorship in Mathematical Physics be created. But then the Irvine Committee came in the way.

The Review Committee appointed by the Viceroy or rather the second Quinquennial Review Committee as it was officially called, consisted of Sir James Irvine, Vice-Chancellor of St. Andrew's University, Dr. A. H. Mackenzie, Pro Vice-Chancellor of Osmania University and Prof. S. S. Bhatnagar. Irvine was born in Glasgow in 1877 and practically grew up with St. Andrew's University, having been associated with it successively as a student, Lecturer, Professor, Dean of the Faculty of Science, Principal and finally Vice-Chancellor. Bhatnagar was at that time in Lahore as the Professor of Chemistry in the Punjab University. As for Mackenzie, he seems to have been included mainly on the strength of his administrative background.

I do not have the time to analyse the findings of the Irvine Committee; those interested in such details may find the same in my book. It suffices to observe that the Irvine Committee did what it was supposed to do, namely, slay Raman.

That this is not an idle accusation becomes evident when one reads a letter written by Max Born to Lord Rutherford in October 1936. After returning to England, Born was

quite silent about the affairs in Bangalore, and it was only when Lord Rutherford insisted that Born decided to speak out. Let me now quote a few passages from Born's letter. Borrowing from Richard Feynman, one can describe this letter as an outsider's inside view of the Institute affairs! This is what Born says in part:

Raman came to the Institute with the idea of making it a centre of science of international standard. What he found was a quiet sleepy place where little work was done by a number of well-paid people. My wife and I met an English couple — the man was a retired official in Ootacamund. When I said I was at the Indian Institute of Science, Bangalore, this man said laughing 'Ah! That is a nice sinecure where people draw high salaries'. Similar expressions we have heard on other occasions. Raman's mere speeding up of the entire pace at the Institute was bound to look like criticism on the former work. Add to this that he made a heavy mistake in not waiting a year or two before starting actual reforms. Naturally he got into troubles with the professors who were at the Institute before him. Two of them left the Institute during the first year — an Indian Mowdawalla, Professor of Electrical Engineering and Watson, Professor of Physical Chemistry. The latter case seems to me one of the main sources of difficulty Raman was to encounter later. Watson's friends and he himself may have expected that he was to be the new Director after Sir Martin retired. Certainly Watson did not like to continue as a Professor under an Indian Director. I was told this by some of his English friends. It is easy now to make the loss of Prof. Watson a point against Raman but it is certainly not just. Openly the real reasons for Watson's leaving the Institute were not known; only the given reason was known, namely, that Raman's manners had driven him away. I know that Raman's manners can cause serious grievances but in Watson's case they were but a pretext.

Elsewhere in the letter Born says:

I want to show you by a few examples that all this is not a matter of mere assumption. Three weeks after us arrived the new Professor of Electrical Engineering Aston at the Institute. Immediately after his arrival the open revolt amongst staff and students began and he became a centre for collecting ever so silly complaints against Raman. We wondered very much till one day Mrs. Aston said to my wife that her husband had been made to accept the post by his English colleagues in charging him with the definite mission to clear up the Institute. Aston had been received in Bombay by the Tatas, had been their guest and got instructions.

Incidentally, Born also points out that Aston failed to get a Professorship in England. About the Irvine Committee, Born observes:

I have no right to criticise the attitude and proceedings of the Committee but I must say that it seemed to me rather surprising. Instead of visiting the Institute and studying the work done in the laboratories, they sat in a government building some four miles away where they behaved like a law court. It was

evident to me from the beginning that they had received instructions beforehand. They examined chiefly Raman's opponents, even students. All the dirty affairs were treated in detail but no voice was raised to take into account the good intentions of Raman or his achievements at the Institute.

Let me now continue with the narration. The Irvine Committee submitted its report in the middle of 1936 and when it was discussed in the Council, Raman was severely attacked for his alleged infringement of rules and procedures. Only three people namely, the Dewan of Mysore, Prof. B. Venkatesachar and Dr. Bawa Kartar Singh spoke on behalf of Raman. Encouraged by the support given by the Council and the adverse report of the Irvine Committee, Raman's opponents now stepped up the campaign and finally on June 1, 1937 Raman wrote to the Chairman of the Council:

Having considered all the circumstances, I feel it would be best that I offer to terminate my contract of service with the Institute as its Director.

Along with his resignation letter, Raman submitted a lengthy memorandum regarding his work at the Institute and defending his actions. The Council resolved that Raman's resignation be accepted, and acceded to his request for a special retirement allowance. It also recorded that the settlement should be regarded as final and amicable. As events transpired, neither was true! In his capacity as the Director, Raman forwarded the Council resolution to the Viceroy and along with it sent a letter of his own. This infuriated the Council which then summoned Raman and revoked its earlier offer. It declared that Raman was unfit to continue any longer as Director and offered him two choices: Either to continue as Professor of Physics or resign with effect from April 1, 1938 on such allowances as he might be entitled to according to standard rules. Raman was also warned that if he declined both options, he would be suspended! There was practically no support from any quarter.

Soon after Raman stepped down, it was widely remarked, including by people well disposed, that while Raman was a brilliant scientist he was a poor administrator. Similar statements were aired in the press during the earlier showdown in Calcutta. These comments do not make any sense when one considers the rich encomiums paid to Raman for his administrative ability while he was in government service. No less a person than the Member for Finance in the Viceroy's Council had written:

We find Venkataraman is most useful for the Finance Department being, in fact, one of our best men.

The truth is not that Raman was a bad administrator but that he was a strong one, a fact not liked by his opponents.

From a historical perspective, I see Raman's struggle as a battle between excellence and mediocrity. Raman championed the cause of excellence but, unlike in fairy tales, he lost. The Council he faced no doubt had men of eminence but alas, they were the legal types who understood little about academic matters or scientific creativity. The handful of people that did, were mostly opposed to Raman on personal grounds.

It is sometimes said that the battle of Kurukshetra is a symbolic representation of the inner conflict we often face. In a similar vein I venture to suggest that Raman's struggle is the paradigm of the battle between excellence and mediocrity which is still going on in most of our laboratories and academic campuses. And alas, as before, excellence is generally continuing to lose.

One of the charges levelled against Raman was that he was antagonistic to applied science. In fact, the Irvine Committee went to town on this subject claiming that while Jamshedji Tata wanted a close association of scientific research with industry, Raman came in the way. In his defence, Raman drew attention to the consultancy he had been offering to the Railways, to his role as an adviser to many princely states concerning their industrialisation programmes, etc. At the same time, he firmly declared that as far as the Institute itself was concerned, it should not become the front-end for industry solving its day-to-day problems like: how to extract more oil, how to make better soap or how to make a particular industrial process more efficient. The Institute was an academic centre aiming to become world-renowned and as such should engage only in those problems which would stimulate the keenest minds. Superior skills are developed only by facing basic challenges. However, the exercise would not be in vain, for such abilities are always useful and available on tap when applications are demanded. Back in 1924, Raman had spent a semester at Caltech as the guest of Robert Millikan and it would seem that he was trying to model the Institute along those lines whereas the Irvine Committee and the Council both wanted it to go in exactly the opposite direction. The crying irony is that after Raman was removed, the Institute did not really do much to promote the industrialisation of the country. As Homi Bhabha pointed out years later, when after Independence we started setting up steel plants, we went abroad shopping for technology although steel plants had been established decades earlier by Tata and by Visweswarayya. Even today we are importing technology left and right. All that has happened is that we have established a string of premier institutes which process our human resources into a commodity called NRIs.

Let me now turn to the scientific contributions which Raman made during his Bangalore period. After he ceased to be the Director, Raman focussed all his attention on research and on building up his Department. Not surprisingly, the prophecy about Bangalore becoming a centre for scientific excellence soon became true. If today Bangalore has emerged as the Science City of the Nation, it is in no small measure due to the seeds sown by Raman half a century ago. Since subsequent speakers are likely to discuss Raman's work in detail, I shall restrict myself to calling attention to a few hardly noticed facts.

One observes that in the Bangalore period, Raman has become more preoccupied than before with natural phenomena. No longer does he seem to set up controlled experiments to test specific principles or theories of physics. Instead aesthetics dominates his attention, and he explores things such as the colour of plumage, the iridescence of shells and of ancient glass, and so on. Even his style seems different. Consider, for example, how he opens his very first paper from Bangalore. He starts:

Great interest naturally attaches to the investigation of the colours that form a striking feature of the plumage of the numerous species of birds. Even a cursory examination, as for instance the observation of the feathers under microscope, shows that the distribution of colour in the material and its optical characters are very different in different cases, indicating that no single explanation will suffice to cover the variety of phenomena met with in practice.

After discussing whether the problem of the origin of colours belongs to the realm of chemistry or physics, Raman directs his attention to the feathers of one particular bird namely, *Coracias indica*. About this bird he says:

This is a species of jay, very common in Southern India, which furnishes readily accessible material for the investigation of this type of colouration of birds. Seen sitting with its wing folded up, *Coracias indica* is not a particularly striking bird, though even in this posture its head, sides and tail show vivid colouration. It is when in flight that the gorgeous plumage of this bird is more strikingly seen and museum specimens of the bird are therefore best mounted with the wings outstretched. The wings then exhibit a succession of bands of colour alternately a deep indigo-blue and light greenish-blue; the tips of the wings show a delicate mixture of both colours.

Raman wrote two papers on shells, the first of which is largely descriptive, being in the style of a naturalist. The papers abound in Latin names seldom seen in a physics journal, and there are delightful descriptions of the shells.

Most people today would tend to conclude that such work is not physics and that Raman had started rambling. My own view is quite different, being based on a detailed study not only of Raman's papers but those of his students as well. If one reads Raman's papers carefully, one will observe a connecting link which is that all these studies relate to the optics of heterogeneous media. While Raman focussed on the natural manifestations of such media, his students explored the more technical aspects. The study of the optical properties of heterogeneous media is highly developed at the present time, and has many practical applications. Unfortunately, the pioneering contributions made by the Bangalore school to the development of this subject are hardly known. It has also escaped notice that these studies are a vindication of Raman's point of view that good applied science is born out of high-class basic research.

During the final phase, Raman spent a good deal of time studying gems and minerals. I have read many of Raman's papers on this subject, and I must confess they left me a bit disappointed on first reading. Some might even wonder whether such papers would get past a referee. Perhaps they might not but that would be too clinical an analysis of the matter. Viewed in a larger perspective, it would appear that during this phase Raman was no longer interested in explaining to others. He had seen, he had understood and he had enjoyed — that was all that mattered. As the poet Keats wrote:

To understand and so become aware,
And, thus, mine beauty from the crystallised air.

It would be too hasty to dismiss these papers as lacking physics. On the contrary, these investigations raised several important questions which were left for Raman's protege Pancharatnam to answer. Crystal optics might have not been fashionable in an age when parity non-conservation was the in thing. But there were certain subtle questions relating to coherence which Pancharatnam exposed and succinctly answered, almost at the same time when others came to similar conclusions *via* the newly emerging topic of quantum optics. Here in Bangalore, Raman and Pancharatnam did not need the maser; good old crystal optics was just as effective. I should also call attention to several papers Raman wrote on internal conical refraction. If that sounds like a topic belonging to the 19th century, then let me mention that Bloembergen investigated precisely this phenomenon in the late seventies, several years after Raman had passed away. Of course, Bloembergen was interested in the nonlinear aspects.

I do not want you to carry the impression that it was all feathers, shells and gems. The Raman-Nath theory and the soft mode about which you will undoubtedly hear later offer adequate proof that at least till the forties, Raman did contribute directly to mainstream physics. It is, however, unfortunate that even these contributions did not always receive the recognition they deserved. I have, for example, seen books on acousto-optics which make no mention of the Raman-Nath papers, although the theory due to them is discussed! There are others who make it appear as if the last word on the subject was said by Brillouin, which is not true.

Why did Raman continue with optics after leaving Calcutta, especially when nuclear physics was the new rage? This is an interesting question. Actually Raman was greatly excited by what was going on at Cavendish and very much wanted to pursue nuclear physics. But alas, he had no money. When Bhabha joined the Institute Raman hoped that the Tatas would make a small grant. The Tatas eventually did, not to Raman but to Bhabha so that he could found the TIFR! However, that is another story. Nevertheless, for a moment one does wonder what might have happened if nuclear physics had struck roots in Bangalore instead of in Bombay. It is said that later in his life Raman often lamented that he should have spent his Nobel Prize money buying a gram of radium instead of investing it on diamonds.

During the last decade, Raman spent much time studying the physiology of vision, a topic to which his boyhood hero Helmholtz had contributed very much. It is an accepted fact that from a scientific point of view, this work of Raman is of no consequence. Raman is often summarily dismissed for having produced theories of dubious value like this one. I do not wish to defend the indefensible but would at the same time like to ask whether it is not conceivable for a person to lose his creativity when repeatedly trampled upon? If this seems far fetched, consider what Abraham Pais says about Einstein:

After that, the creative period ceases abruptly, though scientific efforts continue unremittingly for another thirty years. Who can gauge the extent to which the restlessness of Einstein's life in the 1920's was the cause or the effect of a lessening of creative powers?

The reference is to the violent attacks made on Einstein as a part of Hitler's anti-Semitic campaign. Thus we have here one more famous example of the loss of creativity caused by intemperate personal vilification.

The Raman Institute phase should have been a happy one for Raman as he was now in his own laboratory with independent means and totally free from outside control. Besides, there were interesting problems to study, there were the affairs of the Academy to manage, and last but not the least, there was the wonderful garden to tend to. And yet these were some of the most painful years that Raman spent. Prof. Ramaseshan has given us a poignant description of Raman's agony, comparing his emotions to those of Mahatma Gandhi during the Noakhali disturbances. Why was this so?

In the years immediately after Independence, one witnessed a remarkable scene. We had at the helm of our affairs a great visionary whose centenary we shall be celebrating next year. Unlike the run-of-the-mill leader of the Third World, Jawaharlal Nehru was a profound thinker and held the view that India must emulate the Soviet Union in adopting science and technology as the means of solving her numerous problems. Such a dream had been forming in his mind since the thirties, and now was the time to give shape to those dreams. Thus, science became the magic wand and everybody rallied to Nehru's clarion call. Those were exciting times, thrilling beyond words. Laboratories were established, buildings built, equipment bought, and people hired in large numbers. In no other country was so much sought to be accomplished so rapidly. I vividly recall the magic spell cast on us by Bhabha.

Wasn't this a great experiment and wasn't it to be supported? Yes, thought the whole country, swept as it was by a sense of euphoria. But Raman was troubled. He too wanted poverty banished, he also was in favour of technology and industrialisation, and he was behind no one in his desire to see his country emerge as a powerful nation. However, good science was not created merely by spending money, starting laboratories and by passing orders. More important was the human element, and if in the name of hurry quantity replaces quality then disaster would inevitably follow. To him it seemed that the policies pursued by the government were fraught with danger, however good intentioned they might be. Besides, they appeared to be a negation of all that he had stood and worked for. And so in a characteristic manner he made his objections be known. He was brief, blunt and brusque. As was to be expected, especially in the mood that prevailed, Raman was ignored in official quarters, although his comments made good copy. I myself used to wonder in those days why Raman was objecting to something that appeared to be good. After all he himself had worked for the development of science. So why was he now vigorously protesting? Three-and-a-half decades of service in government have made me wiser and I am now able to see clearly the logic behind Raman's arguments, although he himself chose not to elaborate on it.

As in all countries, funding for science and technology in India has necessarily to come from the government but that does not mean it should come with strings attached. It is a widely accepted fact that the existing governmental framework is not conducive to creativity. Science is a creative endeavour and yet for four decades we have been compelled to work with a totally incompatible system. Government control not only

inhibits creativity, but more disastrously, it encourages sloth and intrigue, besides rewarding non-performance. It is not as if the government and the bureaucracy is composed of ignorant or stupid people. On the contrary, there are many many clever and talented persons in government. And yet we see this amazing contradiction of the government spending a sizeable amount of money in the name of science, etc., on the one hand and preventing achievement by slapping an outmoded system on the other. I have come to the conclusion that barring isolated individuals, the governmental machinery as a whole is indifferent and insensitive to whether our science achieves excellence or not. If specific individuals achieve excellence by overcoming obstacles like Ramanujan and Raman did, for example, they are applauded by the society and the government alike; otherwise scientists as a community are either criticised or ignored. This is a great tragedy, considering the high place given to talent and creativity in our society in earlier eras. Richard Feynman has pointed out in his celebrated report on the Challenger enquiry, that if there is a loss of common interest between the scientists and the management, then calamities are possible. Calamities do not always have to be in the form of a crash; being saddled with a millstone is an equal disaster.

Raman was one of the first to raise his voice against the bureaucratic approach in the post-Independence era, and he did this even though he himself was not subject to the pinch. It is curious that no less a person than Nehru complained about bureaucracy in several of his addresses to the Science Congress. Homi Bhabha did the same in his last public lecture. But bureaucracy has survived, thrived and grown to even more ominous proportions. And there is nobody left now to raise a word of public protest.

I belong to the generation which saw Raman as a fading giant. And our impressions were based on the misconceptions and the biased folklore we were fed with. Having carefully researched his life, I now see how misguided I was. I am sure there must be many other misguided persons like me. Raman was and still is often portrayed as one who did not understand physics. It beats one's imagination how then he could have commanded the respect of giants like Rutherford and Bragg, long before he discovered the Raman Effect. Again, how was he elected a Fellow of the Royal Society as early as 1924 although he did his work in a place so far away from London? How was it that he was asked to open a discussion meeting in Toronto in the early twenties and how come Millikan invited him as a Visiting Professor at Caltech, a post earlier adorned by Lorentz, Sommerfeld and Einstein? When he was appointed to the Palit Chair, it was suggested that Raman should first visit England to receive training. He indignantly refused to visit England for that purpose, although he had not gone abroad even once at that time. How many would pass up a foreign trip today? When he had to step down from the Directorship of this Institute, the press was full of rumours that Raman was planning to settle abroad. With a Nobel Prize in his pocket that should have been quite easy and yet Raman chose to stay behind in his darkest hour. Today, on the other hand, people are dreaming of a green card even while entering college! After retirement, the government offered funds but Raman rejected it even if it meant hardship, so that he could preserve his independence. Can we find such a spirit today? And finally, when he was sounded out for the high office of the Vice-Presidentship, he declined. How many would turn down power and position?

It seems to me that this country has been most fortunate in producing such a spirited scientist who, by his shining example, showed that given courage and tenacity one can achieve against the greatest odds. On the occasion of the Silver Jubilee of the Raman effect, Homi Bhabha wrote that the only purpose of celebrating the anniversary of a great event is to derive inspiration from it. Today we are celebrating another anniversary and I submit that we should derive inspiration from all that this Noble Son of India stood and worked for. Raman made Mahendralal Sircar's dreams come true but unfortunately his own dreams did not. Should we not on this occasion dedicate ourselves to the realisation of that ideal?

Light scattering from condensed matter—Contributions of the Raman school

A. K. SOOD

Department of Physics, Indian Institute of Science, Bangalore 560 012, India.

Received on September 29, 1988.

Abstract

An attempt has been made to highlight some of the contributions of Raman and his coworkers to the field of light scattering from condensed matter. The topics reviewed cover Rayleigh, Brillouin and Raman scattering from a variety of systems—pure liquids, liquid mixtures, colloids, crystals and glasses.

Key words: Light scattering, condensed matter, Raman.

1. Introduction

Light scattering which encompasses Rayleigh, Brillouin and Raman scattering has played a key role in the understanding of static and dynamic properties of condensed matter—be it liquids, crystals, glasses, colloidal suspensions, emulsions or polymers. Professor C. V. Raman published more than 70 papers and his students, collaborators and those who were inspired by him published about 400 papers on various aspects of light scattering from a wide variety of systems¹. The remarkable and pioneering results are too many to be reviewed in this paper, and hence we attempt to highlight only a few of them. All the results presented here are from the pre-laser era. It will be seen that even without lasers which have completely revolutionized and rejuvenated the field of light scattering, Professor Raman and his school made notable contributions—the foremost one, of course, being the discovery of the effect which bears his name.

The scattering of light, in general, occurs due to optical inhomogeneities in the scattering medium. These inhomogeneities can arise due to different reasons, the most obvious case being of gross inclusions of one substance in the other as in colloidal suspensions. The thermodynamic fluctuations of density and temperature (or pressure and entropy), orientations of anisotropic molecules, the fluctuations of concentrations in mixtures or the vibrations of atoms about their equilibrium positions produce fluctuations of dielectric constant of the medium and hence scatter light. The temporal behaviour of different fluctuations is different with time and therefore they modulate the scattered light in different ways.

The entropy fluctuations at constant pressure or the concentration fluctuations do not propagate in the medium and hence result in the Rayleigh scattering unshifted in frequency. The Rayleigh line is, of course, broadened due to the dissipation of the fluctuations. The temperature fluctuations will damp out due to thermal dissipative processes which depend on thermal conductivity and the concentration fluctuations are governed by translational diffusion of the molecules. The orientational fluctuations of the anisotropic molecules dissipate due to rotational relaxation processes.

The fluctuations of density or pressure at constant entropy (adiabatic) represent local compressions or rarefactions which can travel in the medium with velocity of elastic waves. The incident light is scattered due to the grating formed by the periodic stratifications of a particular wavelength governed by the well-known Bragg condition. The propagation of the 'grating' produces Doppler shift of the incident frequency. This view was first put forward by Brillouin² and hence the Doppler-shifted components on either side of the Rayleigh line due to waves travelling in opposite directions but with the same speed are called Brillouin lines. These lines are broadened due to thermal dissipative processes which damp out the elastic waves (sound waves or acoustic phonons).

The fluctuations in the dielectric function can also arise due to the time dependence of some excitations of the medium. These excitations which can be the vibrational modes of a molecule or optical phonons in solids, electronic excitations or magnons in magnetic systems cause inelastic scattering of light called Raman scattering. This was first discovered by Professor C. V. Raman on February 28, 1928 when he pointed a direct-vision spectroscope on to the scattered track in many pure organic liquids and observed the presence of another colour separated from the incident colour^{3,4}. This was the culmination of seven years of intense research by Raman and his many coworkers on light scattering.

The above discussion points out that the spectrum of scattered light contains valuable information on the 'imprints' of different forms of fluctuations in the medium. The four quantities which contain the knowledge of the fluctuations and can be determined experimentally are: (1) the frequency shift (2) the intensity of the scattered radiation (3) spectral linewidth and (4) polarization.

The plan of the paper is as follows. In Section II, we present the important contributions of the Raman school to Rayleigh-Brillouin scattering from liquids, crystals and glasses. Under this heading, the topics to be briefly reviewed are:

- i) Intensity of the total scattered light from the liquids.
- ii) Brillouin scattering from liquids, deviation of intensity ratio of Rayleigh to Brillouin lines from the Landau-Placzek ratio.
- iii) Brillouin scattering from viscous liquids and glasses.
- iv) Light scattering from glasses—the concept of 'frozen-in' fluctuations, depolarization of scattered light in terms of Krishnan ratio, and Brillouin scattering.
- v) Brillouin scattering from crystals.

Section III deals with Raman scattering. A very large number of systems were studied for the first time by Raman and his coworkers to probe structure, symmetry and dynamical properties. We shall not give a catalogue of all those investigations but briefly

discuss only the following: (i) use of Raman spectroscopy in chemical analysis, (ii) resonance Raman scattering, (iii) symmetry and Raman selection rules, (iv) crystal dynamics and (v) phase transitions and the soft mode.

2. Rayleigh-Brillouin scattering from liquids, crystals and glasses

2.1 Scattering from liquids

Historically speaking, Smoluchowski⁵ invoked the idea of density fluctuations to explain the phenomenon of critical opalescence. Later, Einstein⁶ developed the statistical theory of light scattering based on fluctuations in density for a pure liquid along with concentration fluctuations in multi-component systems.

Let I_0 be the intensity of incident light of wavelength λ . The total scattered intensity by a volume element v reaching the detector at a distance L is given by

$$I_s = \frac{I_0 v^2}{L^2} \frac{\pi^2}{2\lambda^4} \langle (\delta\epsilon_q)^2 \rangle (1 + \cos^2 \theta) \quad (1)$$

where $\delta\epsilon_q$ is the q th Fourier component of fluctuations in dielectric constant. The wave-vector $\vec{q} = \vec{k}_i - \vec{k}_s$ and θ is the angle between \vec{k}_i and \vec{k}_s which are the wavevectors of the incident and scattered light. The brackets, $\langle \rangle$, denote the average over the equilibrium ensemble.

Taking ϵ to be a function of pressure P and entropy S ,

$$\langle (\delta\epsilon)^2 \rangle = \left(\frac{\partial \epsilon}{\partial P} \right)_s^2 \langle (\delta P)^2 \rangle + \left(\frac{\partial \epsilon}{\partial S} \right)_P^2 \langle (\delta S)^2 \rangle \quad (2)$$

where subscript q has been dropped for the sake of convenience. We can write

$$\begin{aligned} \left(\frac{\partial \epsilon}{\partial P} \right)_s^2 \langle (\delta P)^2 \rangle &= \left(\frac{\partial \epsilon}{\partial \rho} \right)_s^2 \langle (\delta \rho)^2 \rangle; \\ \left(\frac{\partial \epsilon}{\partial S} \right)_P^2 \langle (\delta S)^2 \rangle &= \left(\frac{\partial \epsilon}{\partial T} \right)_P^2 \langle (\delta T)^2 \rangle; \\ \left(\frac{\partial \epsilon}{\partial T} \right)_P &= \left(\rho \frac{\partial \epsilon}{\partial \rho} \right)_T \alpha_v + \left(\frac{\partial \epsilon}{\partial T} \right)_\rho. \end{aligned} \quad (3)$$

From the theory of thermodynamic fluctuations⁷

$$\langle (\delta \rho)^2 \rangle = \rho^2 k_B T \beta_s / v,$$

$$\langle (\delta T)^2 \rangle = \frac{k_B T^2}{C_P \rho v}. \quad (4)$$

Here ρ and T are density and temperature, β_s the adiabatic compressibility, C_v the specific heat at constant volume, α_v the volume thermal expansion coefficient and k_B the Boltzmann constant. Using eqns (2)–(4) in eqn (1), one gets (for $\theta = 90^\circ$)

$$I_s = \frac{I_0 v}{L^2} \frac{\pi^2}{2\lambda^4} \left[\left(\rho \frac{\partial \epsilon}{\partial \rho} \right)_s^2 \beta_s k_B T + \frac{k_B T^2}{C_p \rho} \left\{ \alpha_v^2 \left(\rho \frac{\partial \epsilon}{\partial \rho} \right)_T^2 + \left(\frac{\partial \epsilon}{\partial T} \right)_\rho^2 \right\} \right]. \quad (5)$$

It can be shown⁸ that if

$$\frac{T \alpha_v^2}{C_p \beta_s \rho} \left[\left(\frac{1}{\alpha_v} \frac{\partial \epsilon}{\partial T} \right)_\rho + \left(\rho \frac{\partial \epsilon}{\partial \rho} \right)_T \right] \ll \left(\rho \frac{\partial \epsilon}{\partial \rho} \right)_T, \quad (6)$$

eqn (5) goes over to the Einstein formula:

$$I_s = \frac{I_0 v}{L^2} \frac{\pi^2}{2\lambda^4} \left(\rho \frac{\partial \epsilon}{\partial \rho} \right)_T^2 \beta_T k_B T, \quad (7)$$

where β_T is the isothermal compressibility.

So far $(\delta \epsilon)$ is taken to be a scalar which is the case when molecules comprising the medium are optically isotropic. On the assumption that molecules are freely rotating, Rayleigh and Gans have shown that the optical anisotropy makes an additional contribution $(6+6r)/(6-7r)$ to the scattering where r is the depolarization ratio given by $r = I_H/I_V$, $I_H(I_V/2)$ is the scattered intensity with polarization parallel (perpendicular) to the scattering plane. The total scattered light due to density and anisotropy fluctuations is given by

$$I_s = \frac{I_0 v}{L^2} \frac{\pi^2}{2\lambda^4} \left(\rho \frac{\partial \epsilon}{\partial \rho} \right)_T^2 \beta_T k_B T \frac{(6+6r)}{(6-7r)}. \quad (8)$$

In order to compare eqn (8) with experiments, it is necessary to know $(\rho \partial \epsilon / \partial \rho)_T$. Einstein used the Lorentz-Lorenz formula connecting ϵ and ρ :

$$\frac{\epsilon - 1}{\epsilon + 2} = C' \rho \quad (9)$$

where C' is a constant. Differencing (9),

$$\left(\rho \frac{\partial \epsilon}{\partial \rho} \right)_T = (\epsilon - 1) \frac{(\epsilon + 2)}{3} \quad (10)$$

After substituting (10) in (9) to get I_s , it was found that the computed scattered intensities are appreciably larger than the measured values. The discrepancy was reduced by Ramanathan⁹. He used the relation, $\epsilon - 1 = (\text{constant})\rho$ by arguing that $(\epsilon + 2)$ in eqn (9) arises due to the action of molecules located outside the small sphere (the Lorentz sphere) surrounding the molecule under observation. The influence of fluctuations of ϵ in the material outside the Lorentz sphere on the change of field inside the sphere will be small and hence the term $(\epsilon + 2)$ can be regarded as constant. Then one gets

$$I_s = \frac{I_0 \cdot \nu}{L^2} \frac{\pi^2}{2\lambda^4} (\epsilon - 1)^2 \beta_T k_B T \cdot \left(\frac{6 + 6r}{6 - 7r} \right) \quad (11)$$

The agreement of eqn (11) with experiments, though satisfactory for a number of liquids, is still not good. Venkateswaran¹⁰ suggested that the limitation involved in adopting any relation between ϵ and ρ is removed by using the experimentally determined values of adiabatic piezoelectric coefficients $(\rho \partial \mu / \partial \rho)_s$ (μ = refractive index = $\sqrt{\epsilon}$) obtained by Raman and Venkataraman¹¹. The contributions of Krishnan¹², Raman and Rao¹³, Ramanathan¹⁴ and Ananthakrishnan¹⁵ are noteworthy for the measurements of scattered intensities in a number of liquids. Rao¹⁶ investigated the dependence of the scattered intensities on temperature for liquids and interpreted his results in terms of eqn (11).

Raman and Krishnan¹⁷, and Cabannes and Daure¹⁸ discovered that a depolarised continuous background appears which extends out $\sim 150 \text{ cm}^{-1}$ from the unshifted line and even further. This arises as result of the rapid temporal changes of the fluctuations of the anisotropy. In recent times, this broad wing has been investigated extensively to study rotational-relaxation mechanisms.

2.2 Brillouin scattering from liquids and Landau-Placzek ratio

As mentioned in the introduction, the density fluctuations at constant entropy give rise to Brillouin lines shifted by frequency

$$\omega_B = \pm \nu_e q \quad (12)$$

where ν_e is the appropriate sound velocity and $q = (4\pi\mu \sin \theta/2)/\lambda$. Here μ is the refractive index of the medium.

The sum of the intensities ($2I_B$) of the two Brillouin components is given by the first term in eqn (5) and the other terms in the equation contribute to Rayleigh line intensity (I_R). Landau and Placzek¹⁹ showed that, under certain assumptions,

$$\frac{I_R}{2I_B} = \frac{\beta_T - \beta_s}{\beta_s} = \frac{C_p - C_v}{C_v} = \gamma - 1. \quad (13)$$

Even though the prediction of the shifted lines was made by Brillouin² in 1922, the first experimental observation was made by Gross²⁰ in liquids after the discovery of the Raman Effect. Krishnan²¹ in his review article on Brillouin scattering mentions that the

most satisfactory patterns of the Doppler-shifted Brillouin components in liquids were recorded by Rao²². Extensive work was done by Venkateswaran²³ and Sunanda Bai²⁴.

Venkateswaran²³ was the first to demonstrate the failure of Landau-Placzek relation, eqn (13), in many liquids. Cummins and Gammon²⁵ attributed this discrepancy due to the neglect of dispersion of the thermodynamic quantities in the hypersonic region. The quantities involved in the expression for I_R correspond to the static value ($\omega = 0$) whereas the quantities in $2I_B$ should be those in the hypersonic frequency range ($\omega \sim 10^{10}$ Hz). The correction for the dispersion does not remove the discrepancy completely, the observed $I_R/2I_B$ is always higher than the theoretical values²⁵. For example, the observed value of $I_R/2I_B$ in benzene is 0.84, eqn (13) gives 0.43 and after correction for dispersion, it is 0.66.

The relatively small calculated values of $I_R/2I_B$ point out that there are other mechanisms contributing to the Rayleigh intensity. These can be understood in the hydrodynamic theory of light scattering by Mountain²⁶. He pointed out that the spectral distribution contains a non-propagating mode in addition to the usual thermal and phonon modes which give rise to the central and two shifted-Brillouin components. This new mode called the fourth component arises from the exchange of energy between the internal vibrational modes and translation modes of the molecules and dissipates with relaxation time τ . It gives rise to the appearance of a broad line of unshifted frequency with a width $\Delta\omega_{FC} \approx \tau^{-1}$ and integrated intensity $(1 - v_0^2/v_\infty^2)\gamma^{-1}$, where v_0 and v_∞ are the low- and high-frequency sound velocities. The fourth component is polarised in the same plane as the Brillouin components. Figure 1 shows a schematic of the spectrum of scattered light. The presence of the fourth component also makes Brillouin lines asymmetric, and this can depend on temperature due to the dependence of the relaxation time τ (and hence $\Delta\omega_{FC}$) on T . Since the fourth component is mainly present over the central component, the measured ratio of $I_R/2I_B$ will be higher than that estimated from eqn (13) even after applying correction for the dispersion.

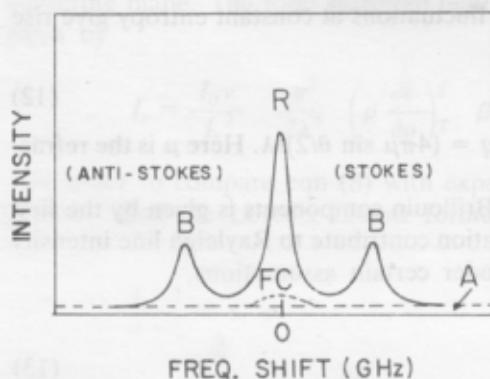


FIG. 1. Schematic illustration of the spectrum of the scattered light from a liquid. R and B stand for Rayleigh and Brillouin components. A is the background due to orientational fluctuations and FC is the fourth component proposed by Mountain²⁶.

Knapp *et al*²⁷ have argued that in addition to the thermal relaxation process introduced by Mountain in frequency-dependent bulk viscosity, other relaxation processes described by frequency-dependent shear viscosity or elastic moduli would give rise to velocity dispersion and hence to the presence of the fourth component. Their experiments on glycerine as a function of temperature show that the broad intense background arises due to the structural relaxation occurring predominantly in associated liquids (which tend to form ordered molecular aggregates over various volumes).

2.3 Brillouin scattering from viscous liquids and glasses

A finite damping of the sound waves in a viscous medium contributes to the linewidth, $\Delta\omega_B$, of the Brillouin lines^{8,19}:

$$\Delta\omega_B = \Gamma q^2 = 2\alpha v_e \quad (14)$$

where

$$\Gamma = \frac{1}{\rho} \left[\frac{4}{3} \eta_s + \eta_v + \frac{\sigma}{C_p} (\gamma - 1) \right]. \quad (15)$$

Here η_s and η_v are the shear and bulk viscosities, σ the thermal conductivity and α the absorption coefficient for the sound waves in the medium. The term $\sigma(\gamma-1)/C_p$ is usually very small as compared to viscosity terms in eqn (15). The peak of the Brillouin line is also shifted from ω_B given by eqn (12) as

$$\omega'_B = (\omega_B^2 - 2\alpha^2 v_e^2)^{1/2}. \quad (16)$$

It appears that when η_v and η_s are large (in viscous liquids), $\Delta\omega_B$ will be very large and the shift ω'_B will go to zero, suggesting that the Brillouin lines should not be seen in viscous liquids and glasses. Contrary to this, Venkateswaran²³ observed the Brillouin lines in a number of viscous liquids, including glycerine and castor oil. The shifted components were seen in glycerine up to a viscosity of 120.4 poise and for castor oil, up to 6.04 poise (for comparison, the viscosity of water at room temperature is ~ 0.01 poise).

A number of unsuccessful attempts were made before 1950 by Gross, Ramm, Raman and Rao, Venkateswaran, Velichkina, and Rank and Douglas to detect Brillouin lines in glasses. The first successful observation was reported by Krishnan²⁸ in fused quartz by using 2536 Å excitation from mercury vapour lamp. The Brillouin shift was $\pm 1.5 \text{ cm}^{-1}$ which agreed well with the calculated $\pm 1.65 \text{ cm}^{-1}$ from the elastic constants.

Let us now see how we can qualitatively understand Venkateswaran's observations in viscous liquids and Krishnan's result on fused quartz. The argument that the absorption coefficient α is proportional to the viscosity η cannot be valid for the entire range of η because, if this were the case, the glasses (for which $\eta \sim 10^{13}$ poise) cannot be good conductors of sound. In reality, glasses are good conductor of sound even at high frequencies. This happens because of the relaxation processes due to which α increases with increase in viscosity up to a definite maximum, after which it falls off with continued in-

crease in η . The difficulty in detecting Brillouin lines in earlier observations can be understood by realising that $I_B \propto \beta_s$ [see eqn (5)] and $\beta_s = (\rho v_{HS})^{-1}$ where v_{HS} is the hypersonic velocity. In relaxation theory, at higher frequencies ($\omega\tau \gg 1$) when a system with a large value of η relaxes, $v_\infty - v_0$ will also be large *i.e.*, the liquid will behave like a solid at high frequencies. The large dispersion in velocity will make β_s and hence I_B small as compared to that in the low-viscous liquids.

2.4 Light scattering from glasses

In this section, we shall highlight the fundamental contributions in the following: i) Concept of 'frozen-in' fluctuations in glasses; and ii) Krishnan Effect.

2.4.1 'Frozen-in' fluctuations in glasses

Young Rayleigh²⁹ (John William Strutt) conjectured that accidental inclusions and incipient crystallization occurring within the glass were responsible for scattering the light. It was first shown by Raman³⁰ that light scattering from glasses has its origin in true molecular scattering arising from local fluctuations of composition and of molecular orientation, as in a liquid. He arrived at this important conclusion after measuring scattered intensities for fourteen different types of silicate glasses with refractive indices varying from 1.4933 to 1.7782. The measured intensities relative to liquid benzene varied from 0.11 to 0.63 while the depolarization ratio ranged from 0.045 to 0.295. Raman's conclusions were reinforced later by Krishnan³¹, Krishnan and Rao³², Rank and Douglas³³, Debye and Bueche³⁴ and Maurer³⁵.

In all these studies, it was found that the value of the measured scattered intensity is almost an order of magnitude larger than the calculated intensity on the basis of equilibrium density fluctuations. Raman³⁰ proposed that the increased measured intensity was due to the 'freezing-in' (thermal arrest) of concentration fluctuations. Later, Müller³⁶ extended this idea to the 'frozen-in' density fluctuations. Fabelinskii⁸ has quoted the work of Vladimirskii (in 1940) which suggested the possibility of freezing of orientation fluctuations. In order to amplify the above point regarding the discrepancy between the observed and calculated intensities, we shall quote the results of Velichkina on fused quartz as reported by Fabelinskii⁸.

The measured scattering coefficient R , defined as $R = I_s L^2 / I_0 v$, for fused quartz in transverse direction ($\theta = 90^\circ$) at a temperature of -70°C was $1.86 \times 10^{-6} \text{ cm}^{-1}$. In order to calculate the scattered intensity, glass was considered either as a liquid or as a crystal with an infinite number of symmetry axes. Using eqn (8) and taking T to be the temperature of measurements, Velichkina estimated $R = 2.3 \times 10^{-7} \text{ cm}^{-1}$. The scattering coefficient for the cubic crystal for the transverse scattering, when incident light is unpolarized, is given by⁸

$$R = \frac{\pi^2}{2\lambda^4} \mu^8 k_B T \cdot \left[\frac{p_{12}^2}{C_{11}} + (p_{11} - p_{12})^2, \right. \\ \left. \left\{ \frac{1}{4C_{11}} + \frac{1}{2(C_{11} - C_{12})} \right\} \right] \quad (17)$$

This expression was obtained by Leontowitsch and Mandelstamm in 1932. Here C_{ij} are the elastic constants and p_{ij} are Pockel's elasto-optical constants. The first term, p_{12}^2/C_{11} , arises due to density fluctuations and the other terms are due to anisotropy or orientation scattering. For isotropic solid, $p_{11} - p_{12} = 2p_{44}$ and $C_{11} - C_{12} = 2C_{44}$. Using eqn (17), Velichkina calculated $R = 1.8 \times 10^{-7} \text{ cm}^{-1}$ for fused quartz. Therefore, the calculated scattering coefficients for fused quartz using either liquid state theory or based on crystals are an order of magnitude larger than the measured value.

2.4.1.1 Freezing-in density fluctuations

Applying this idea to fused quartz, Velichkina assumed that the scattering in fused quartz is determined by the density fluctuations close to the glass-transition temperature $T_g \sim 2100 \text{ K}$. Then, using eqn (8) and taking $T = T_g$, $R = 1.5 \times 10^{-6}$, is in good agreement with the experiment.

The density fluctuations can be either isobaric or adiabatic:

$$\langle (\delta\rho)^2 \rangle = \left(\frac{\partial\rho}{\partial S} \right)_P^2 \langle (\delta p)^2 \rangle + \left(\frac{\partial\rho}{\partial P} \right)_S^2 \langle (\delta S)^2 \rangle. \quad (18)$$

The isobaric density fluctuations are dissipated with a time-constant

$$\tau_p = (\chi q^2)^{-1} \quad (19)$$

where $\chi = \sigma/\rho C_p$ is the thermal diffusivity. For visible light and $\theta = 90^\circ$, $q \sim 5 \times 10^5 \text{ cm}^{-1}$ and taking for glasses, $\chi \sim 3 \times 10^{-3} \text{ cm}^2/\text{s}$, $\tau_p \sim 10^{-9} \text{ s}$. Hence the isobaric fluctuations of the density are quite fast and it is likely that such fluctuations may or may not freeze during cooling.

The adiabatic fluctuations of density move with the speed of hypersound (giving rise to Brillouin scattering). From the fact that Brillouin components exist in glasses²⁸, the freezing of adiabatic density fluctuations is clearly ruled out.

2.4.1.2 Freezing-in concentration fluctuations

The time constant associated with the concentration fluctuations is

$$\tau_c = (Dq^2)^{-1} \quad (20)$$

where D is the diffusion coefficient. For ordinary liquids, $D \sim 10^{-5} \text{ cm}^2/\text{s}$ and hence $\tau_C \sim 10^{-10} \text{ s}$. But near the glass-transition temperature, D decreases by many orders of magnitude (recall $D \propto 1/\eta$). Taking $D \sim 10^{-9} \text{ cm}^2/\text{s}$, $\tau_C \sim 10^{-3} \text{ s}$ and hence one can expect the arrest of the concentration fluctuations in liquid to glass transition.

2.4.1.3 'Fictive temperature' in a glass

The concept of frozen-in fluctuations proposed by Raman is one of the key points in glass physics. The introduction of a 'fictive temperature'^{37,38} is a useful concept. At a fictive temperature T_f , density fluctuations are arrested so that upon lowering the temperature further no structural rearrangement is possible. Therefore, T_f becomes the governing temperature for the molecular structure of a glass. Another fictive temperature T'_f is associated with thermally arrested concentration fluctuations, and in general, $T'_f \neq T_f$. Since $\tau_C \gg \tau_p$, concentration fluctuations are 'arrested' at a relatively higher temperature than the density fluctuations *i.e.*, $T'_f > T_f$. Usually, T_f is taken³⁷ to be the temperature at which the liquid viscosity is $\sim 10^{13.5}$ poise or the glass-transition temperature T_g . Typically, $\tau_C/\tau_p \sim 10^6$ and therefore T'_f may be taken to be the temperature at which the liquid viscosity is $\sim 10^7 - 10^8$ poise³⁹.

2.4.2 Krishnan Effect

The Krishnan Effect, discovered by R. S. Krishnan, relates to the state of polarization of the scattered radiation by condensed matter in a direction normal to the incident beam. As shown in fig. 2, four possible scattering intensities can be measured: $I_s(\text{VV})$, $I_s(\text{VH})$, $I_s(\text{HV})$ and $I_s(\text{HH})$, where H and V refer to the polarization parallel and perpendicular

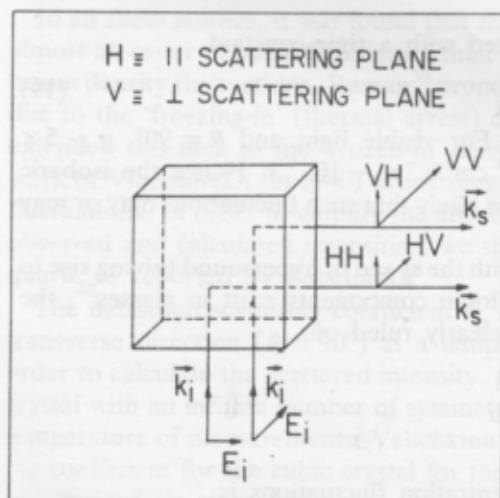


FIG. 2. Schematic representation of the polarized components of the scattered light.

to the scattering plane, respectively. The first letter in brackets (e.g., V in $I_s(\text{VH})$) refer to the polarization of the incident radiation and the second one corresponds to the polarization of the scattered radiation. The depolarization ratios are defined by

$$\rho_H = \frac{I_s(\text{HV})}{I_s(\text{HH})} \quad (21)$$

and

$$\rho_V = \frac{I_s(\text{VH})}{I_s(\text{VV})} \quad (22)$$

The relation $I_s(\text{VH}) = I_s(\text{HV})$ is true for all materials (not optically active) and is called Rayleigh-reciprocity relation as was shown by Krishnan⁴⁰.

For isotropic fluids consisting of molecules with dimension much less than wavelength of light,

$$I(\text{VH}) = I(\text{HV}) = I(\text{HH}).$$

The Krishnan Effect is the observation that in a number of liquids and solids,

$$\rho_H < 1. \quad (23)$$

The Krishnan Effect has been demonstrated for critical liquid mixtures, associated liquids like formic and acetic acids, emulsions, colloids, proteins⁴⁰⁻⁴⁶, cholesteric liquid crystals⁴⁷ and a number of glasses^{31,39,48,49}. The effect observed in colloids could be explained with Mie theory of light scattering from medium consisting of non-spherical particles (or 'clusters') with linear dimensions of the order of wavelength of incident light wherein the phase differences between the waves emitted from different points of the particle must be taken into account. It may be noted that the intensities referred to in ρ_H are for the unshifted component (Rayleigh) as the Brillouin components are very weak in these systems.

There have been a number of attempts to understand Krishnan Effect in glasses. Prompted by the effect in colloids, Krishnan proposed that there are 'clusters' of dimension $\sim \lambda$ in glasses which scatter light. Gans⁵⁰ gave a theory based on the optical anisotropy of clusters which have to be necessarily strongly aspherical. Gans' theory⁵⁰ usually predicts $\rho_H > 1$ in contrast to the observation that $\rho_H < 1$. The next theoretical work was that of Müller³⁶ who questioned the cluster hypothesis of Krishnan in light of the X-ray investigation of Warren. Müller proposed a theory of Krishnan Effect based on strain scattering in glasses in which it is assumed that the equipartition of energy is not obeyed. The strain energy is stored more in the longitudinal modes than in the transverse modes. The Krishnan ratio becomes

$$\rho_H = \frac{U_T}{U_L} \frac{C_{11}}{2C_{44}} = \frac{U_T}{U_L} \frac{(1-\sigma_P)}{(1-2\sigma_P)} \quad (23)$$

where U_T and U_L are the energy densities of the transverse and the longitudinal strain waves and σ_P the Poisson ratio. If the equipartition energy principal is used, $U_T = U_L = k_B T/2v$ then $\rho_H = C_{11}/2C_{44}$ which is the same as in an isotropic solid. To explain $\rho_H < 1$, Müller argued that $U_L = k_B T_f/2v$ and $U_T < U_L$. This assumption is definitely unappealing because the transverse waves should as well play an important role as the longitudinal waves in the glass transition. Further, for glasses like fused quartz³⁹, $\rho_H \sim 1$. Müller theory does not specify on what grounds one expects $\rho_H \sim 1$ in some glasses. Further, according to theory³⁶,

$$\rho_V = \frac{1}{4} \frac{U_T}{U_L} \left(\frac{1 - \sigma_P}{1 - 2\sigma_P} \right) \cdot \left(1 - \frac{q}{P} \right)^2 \quad (24)$$

where q and p are Neumann's constants related to p_{ij} by $p_{11} = 2q/\mu$, $p_{12} = 2p/\mu$. From eqns (23) and (24),

$$\frac{\rho_V}{\rho_H} = \frac{1}{4} \left(1 - \frac{q}{P} \right)^2. \quad (25)$$

In general, $q < p$ and, therefore, the maximum value of ρ_V/ρ_H is 0.25 in Müller's theory. The experimental results on many glasses^{48,49} do not agree with eqn (25).

Schroeder³⁹ has established a connection between concentration fluctuations and the Krishnan Effect by measuring ρ_H in a number of $xK_2O \cdot (100-x)SiO_2$ and $xNa_2O \cdot (100-x)SiO_2$ glasses. Figure 3 shows his data on ρ_H versus x . The minima in ρ_H mostly arises from a pronounced maxima in $I_s(HH)$ rather than any anomalous behaviour in $I_s(VH)$ ^{39,48,49}. The above silicate glasses undergo phase separation as a function of temperature and it has been observed that ρ_H is the minimum at those concentrations of alkali oxides which are close to the critical composition. This establishes that $I_s(HH)$ reflects some aspect of the critical phase-separation process. This is further corroborated

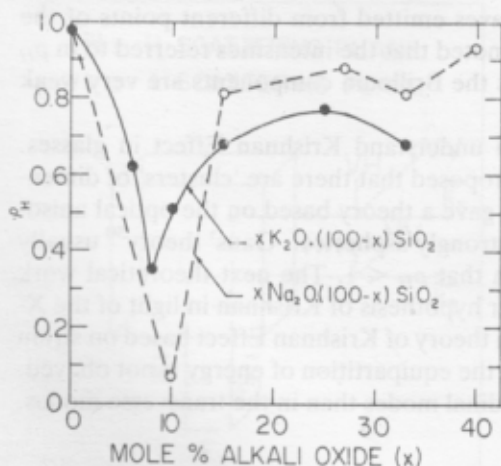


Fig. 3. Krishnan ratio ρ_H versus concentration of alkali oxides in glasses. Data are taken from Schroeder's work³⁹.

by Schroeder by observing that ρ_H increases from ~ 0.2 to ~ 0.5 as $(T - T_s)$ is increased from 50 to 150°C (here T is the temperature at which each particular sample was heat-treated and T_s is the spinodal temperature). Schroeder has suggested that the isotropic composition fluctuations (described by a scalar) which increase near the critical temperature must be coupled to the longitudinal 'frozen-in' fluctuations of the dielectric susceptibility (a tensorial quantity) and a mode-mode coupling approach may provide the key to the Krishnan Effect.

The effect in the glassy state of polybutadiene and polypropylene glycol has been attributed to the frozen-in fluctuations of the anisotropy^{48,49}.

2.5 Brillouin scattering from crystals

In a crystal, three pairs of Doppler-shifted components can occur due to three types of elastic waves which can propagate with different velocities in any general direction. For a symmetry direction the waves can be pure longitudinal or pure transverse. The Brillouin lines were first observed in a solid like quartz by Gross⁵¹ and later by Raman and Venkateswaran⁵² in gypsum. Chandrasekharan⁵³ showed that for a birefringent crystal, there should be twelve Doppler components. A number of crystals like diamond, calcite and alkali halides were studied by Krishnan and coworkers²¹.

3. Raman scattering

Contributions of Indian scientists to Raman spectroscopy have been reviewed recently by Krishnan⁵⁴. We shall mention here only a few of them.

3.1 Use in chemical analysis

The extensive use of Raman spectroscopy in chemical analysis is based on the fact that every chemical bond in a molecule has its characteristic Raman fingerprints which are not affected much by the other parts of the same molecule. By examining a homologous series of compounds commencing from its earlier member, it is possible to trace the development of Raman spectra with increasing complexity of the molecule and to locate these frequencies which are characteristic of particular groups or linkages. This important conclusion was reached by Bhagavantam, Venkateswaran and Ganesan along with others like Dadien and Kohrausch (for detailed references, see the review article by Bhagavantam⁵⁵).

3.2 Resonance Raman scattering

When the incident radiation is close to an electronic transition in the medium, the Raman cross-section shows an enormous enhancement, defying the usual ν^4 law. This is called resonance Raman scattering and was discussed by Placzek in his masterly theory of Raman scattering⁵⁶. With the advent of tunable dye lasers, resonance Raman scattering has become an important technique to understand electron-phonon interactions in crystals, especially semiconductors⁵⁷, and in conformational analysis of biomolecules.

The first observations which gave clear indication of resonance enhancement were made by Sirkar⁵⁸ in CCl_4 and nitrobenzene. He also showed that the depolarization characteristics of the Raman lines also change as the incident radiation frequency approaches the absorption frequency in liquids.

3.3 Symmetry and Raman selection rules

A vibration is said to be Raman active when it produces a change of polarizability in the vibrating system. The deformations produced by the vibrations in the polarizability ellipsoid of the crystal depend upon the symmetry of the given vibration and the symmetry of the crystal. Placzek⁵⁶ has given tables of selection rules for various types of vibrations belonging to any of the 32 point groups of crystal symmetry. However, Saxena⁵⁹ gave a lucid exposition of the subject based on the geometrical reasoning and cleared up certain discrepancies between the theoretical works of Placzek and Cabannes who give different tensors for degenerate vibrations in systems possessing only one axis of three-fold symmetry. Pioneering work was done by Bhagavantam and Venkatarayudu who gave a clear group-theoretical analysis of vibrations in crystals based on the unit-cell approach^{60,61}.

3.4 Crystal dynamics

Due to wavevector conservation, phonons near the Brillouin-zone centre ($q \sim 0$) can participate in the first-order Raman spectra and hence the detailed nature of the phonon-dispersion curves is not probed. In the second-order Raman scattering, however, two phonons of equal and opposite wavevectors, anywhere in the Brillouin zone, can participate. Hence the second-order spectra (SORS) consisting of a continuous background extending over a wide frequency range with sharp peaks superimposed on it are much more rich in information and have an important bearing on the theories of lattice dynamics. High-quality SORS were recorded by Krishnan for diamond, rock salt and alkali halides⁶²⁻⁶⁵. Prompted by this, Born and Bradburn⁶⁶ applied the Born-von Karman theory of lattice dynamics to calculated SORS of rock salt. Later, Birman⁶⁷ and Loudon⁶⁸ have pointed out the importance of van-Hove singularities in the one-phonon densities of states to explain the peaks in the intensity distributions of SORS.

Another important observation is in SORS of diamond by Krishnan⁶⁵. Figure 4 shows the microphotometer record of the Raman spectra of diamond⁶⁵. The peak at 1332 cm^{-1} is the first-order Raman mode. What is of significance is that the sharp peak at 2666 cm^{-1} observed in the second-order Raman spectra lies higher than twice the first-order line. Later, Solin and Ramdas⁶⁹ reexamined the Raman spectra of diamond with improved experimental accuracy using lasers and confirmed the results of Krishnan and also obtained temperature and polarization characteristics of 2666 cm^{-1} mode. These results prompted Cohen and Ruvalds⁷⁰ to propose the existence of two-phonon bound state which can be split off the top of the two-phonon continuum by anharmonic phonon-phonon interactions.

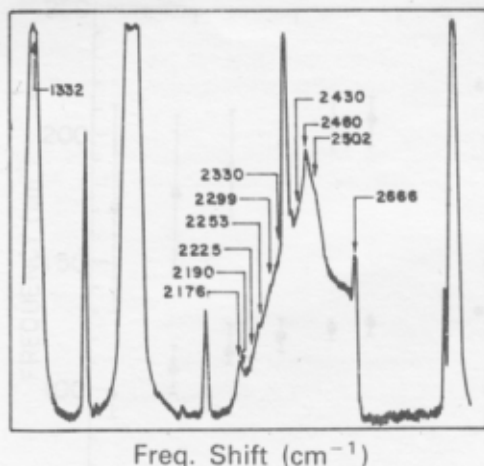


FIG. 4. Microphotometer record of the Raman spectrum of diamond (after Krishnan)⁶⁵.

3.5 Phase transitions and 'soft mode'

The study of phase transitions has been one of the most pursued branch in condensed-matter physics. The concept of 'soft mode', formally proposed by Cochran⁷¹ in 1959 but discovered much earlier by Raman and Nedungadi⁷² in 1940, has played an increasingly dominant role in the understanding of solid-state phase transitions⁷³. What is a soft mode? A soft mode is a collective excitation which may be either propagating or diffusive, whose frequency decreases substantially as the transition temperature T_0 (or pressure) is reached from above or below. Figure 5 shows the schematic behaviour of the soft mode for first- and second-order phase transitions. The static atomic displacements occurring in going from one phase to the other represent the frozen-in mode displacements of the unstable phonon.

The question of structural phase transition as the limit of stability against a particular mode of vibration was formally discussed by Cochran⁷¹. The basic idea and the first observation of the soft-mode were made by Raman and Nedungadi⁷² in their Raman investigations of a solid-state structural phase transition from α (trigonal) to β (hexagonal) phase at $\sim 573^\circ\text{C}$ in crystalline quartz. They observed that "The 220 cm^{-1} line behaves in an exceptional way, spreading out greatly towards the exciting line and becoming a weak diffuse band as the transition temperature is approached". Realising the importance of their results, they proposed that "The behaviour of the 220 cm^{-1} line clearly indicates that the binding forces which determine the frequency of the corresponding mode of vibration of the crystal lattices diminishes rapidly with rising temperature. It appears therefore reasonable to infer that the increasing excitation of this particular mode of vibration with rising temperature and the deformations of the atomic arrangement resulting therefrom are in a special measure responsible for the remarkable changes in the properties of the crystal as well as for inducing the transformation from the α to the β form". This is an exceedingly beautiful description of a soft

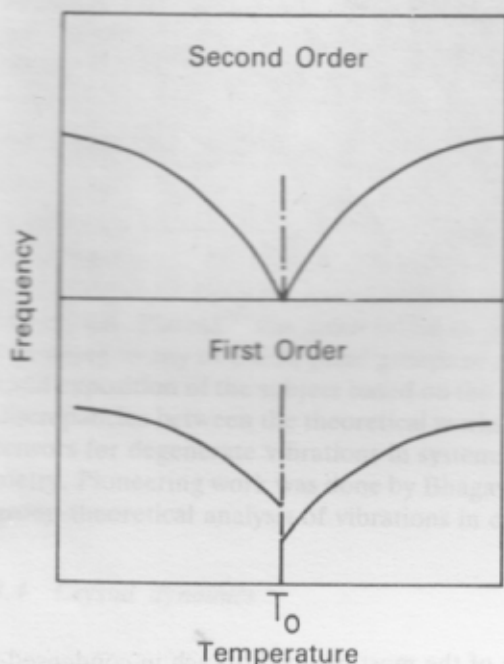


FIG. 5. Schematic representation of variation of soft-mode frequency with temperature for first- and second-order phase transitions.

mode, almost twenty years ahead of Cochran's work. Saxena⁷⁴ carried out a lattice dynamic calculation of quartz and showed that one particular mode was unstable.

Figure 6 shows the data of Nedungadi⁷⁵ for α -quartz for two modes. The bars indicate the lower and upper limits of the Raman lines. Earlier it was confusing that the two modes at $\sim 220 \text{ cm}^{-1}$ and $\sim 147 \text{ cm}^{-1}$ show anomalous temperature dependence. Also, the 147 cm^{-1} was present in polarized α_{zz} -Raman spectra, in addition to the four modes predicted by group theory. The unambiguous assignment of this extra mode as the second-order (two-phonon) process was made by Scott and Porto⁷⁷. Scott⁷⁶ showed that the soft-mode at $\sim 220 \text{ cm}^{-1}$ interacts very strongly with the two-phonon state via anharmonic interaction (Fermi-resonance). The soft-mode in quartz is then the feature at $\sim 40 \text{ cm}^{-1}$ close to T_0 . The temperature dependence of the uncoupled mode deduced by Scott along with his data on quartz are shown in fig. 7. The soft-mode behaviour goes as $\omega \sim A(T_0 - T)^{0.3}$.

The concept of soft-mode initially given for the displacive phase transitions has been extended to order-disorder transitions like in hydrogen-bonded ferroelectrics. The soft-collective excitations in order-disorder transitions are not phonons but rather unstable pseudo-spin waves which occur in addition to all the phonon modes predicted by harmonic theory of crystal lattices. Further, the idea of lattice-vibrational soft-mode has been generalised by Schneider *et al*⁷⁸ to several other phase transitions (like superfluid transition) by combining the static aspects of phase transitions with the dynamic

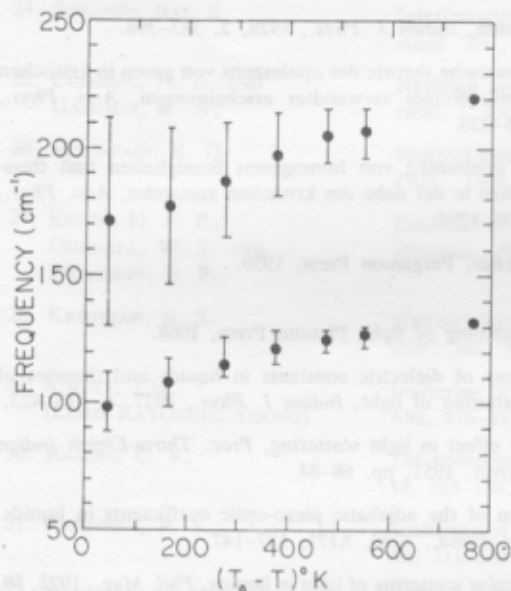


FIG. 6. Temperature dependence of modes in α -quartz. Data are taken from Nedungadi⁷⁵.

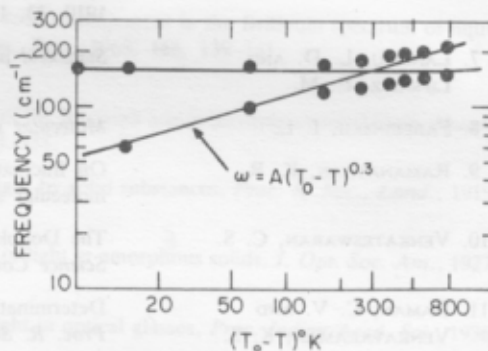


FIG. 7. Temperature dependence in α -quartz from the work of Scott⁷⁷. The solid lines show the temperature dependence of uncoupled modes.

response of the system. To summarize, the concept of the soft-mode provides a unified view of the phase transitions and hence the early work of Raman and Nedungadi assumes a significant place in the study of the phase transitions.

4. Conclusion

We have attempted to bring out a few important contributions of Raman and his co-workers in all the fields of light scattering from condensed matter. Limitations of space did not allow us to include the interesting work of Raman and Ramdas on the scattering of light at the interface between two media and the famous Raman-Nath theory of diffraction of light by sound waves. Nor could we include post-laser work on the Raman study of ferroelectric phase transitions by P. S. Narayanan and his group.

To conclude, the work of Raman school on light scattering remains a guiding spirit in many of the present-day researches in condensed-matter physics.

References

1. RAMAN, C. V. *The scattering of light—The scientific papers of Sir C. V. Raman*, The Indian Academy of Sciences, Bangalore, 1978.
2. BRILLOUIN, L. *Ann. Phys. (Paris)*, 1922, **88**, 17.
3. RAMAN, C. V. AND KRISHNAN, K. S. A new type of secondary radiation, *Nature*, 1928, **121**, 501–502.

4. RAMAN, C. V. A new radiation, *Indian J. Phys.*, 1928, **2**, 387-398.
5. SMOLUCHOWSKI, M. Molekular-kinetische theorie der opaleszenz von gasen in kritischen zustande, sowie einiger verwandter erscheinungen, *Ann. Phys.*, 1908, **25**, 205-226.
6. EINSTEIN, A. Theorie der opaleszenz von homogenen flussigkeiten und flussigkeitsgemischen in der nahe des kritischen zustandes, *Ann. Phys.*, 1910, **33**, 1275-1298.
7. LANDAU, L. D. AND LIFSHITZ, E. M. *Statistical physics*, Pergamon Press, 1959.
8. FABELINSKII, I. L. *Molecular scattering of light*, Plenum Press, 1968.
9. RAMANATHAN, K. R. On fluctuations of dielectric constants in liquids and theories of molecular scattering of light, *Indian J. Phys.*, 1927, **1**, 413-423.
10. VENKATESWARAN, C. S. The Doppler effect in light scattering, *Proc. Thirty-Eighth Indian Science Congress*, 1951, pp. 68-84.
11. RAMAN, C. V. AND VENKATARAMAN, K. S. Determination of the adiabatic piezo-optic coefficients in liquids, *Proc. R. Soc. Lond.*, 1939, **A171**, 137-147.
12. KRISHNAN, K. S. On the molecular scattering of light in liquids, *Phil. Mag.*, 1925, **50**, 697-715.
13. RAMAN, C. V. AND RAO, K. S. On the polarization of the light scattered by gases and vapours, *Phil. Mag.*, 1923, **46**, 426-434.
14. RAMANATHAN, K. R. The molecular scattering of light in vapours and in liquids and its relation to the opalescence observed in the critical state, *Proc. R. Soc. Lond.*, 1922, **102**, 151-161.
15. ANANTHAKRISHNAN, R. Photoelectric photometry of light scattering in fluids, *Proc. Indian Acad. Sci.*, 1934, **A1**, 201-210.
16. RAO, R. *Indian J. Phys.*, 1927, **2**, 7.
17. RAMAN, C. V. AND KRISHNAN, K. S. Molecular spectra in the extreme infrared, *Nature*, 1928, **122**, 278, 882.
18. CABANNES, J. AND DAURE, P. Analyse spectroscopique de la lumiere obtenue par diffusion moleculaire d'une radiation monochromatique au sein d'un fluide, *Comptes Rendus*, 1928, **186**, 1533-1534.
19. LANDAU, L. D. AND LIFSHITZ, E. M. *Electrodynamics of continuous media*, Addison-Wesley, 1960.
20. GROSS, E. Uber anderung der wellenlange bei lichtzerstreuung in kristallen, *Z. Physik*, 1930, **63**, 685-687.
21. KRISHNAN, R. S. Brillouin scattering in *The Raman Effect* (ed. A. Anderson), 1971, pp. 41-404, Marcel Dekker.
22. RAO, B. V. R. Examination of molecularly scattered light with a Fabry-Perot etalon, *Proc. Indian Acad. Sci.*, 1934, **A1**, 261-268, 473-483, 765-767; 1935, **A2**, 236-241.
23. VENKATESWARAN, C. S. Interferometric studies of light scattering in mobile liquids, viscous liquids and glasses, *Proc. Indian Acad. Sci.*, 1942, **A15**, 322-337, 362-370, 371-375.

24. SUNANDA BAI, K. Interferometric studies of light scattering in liquids, *Proc. Indian Acad. Sci.*, 1942, **A15**, 349-356, 357-361.
25. CUMMINS, H. Z. AND GAMMON, R. W. Rayleigh and Brillouin scattering in liquids—The Landau-Placzek ratio, *J. Chem. Phys.*, 1966, **44**, 2785-2796.
26. MOUNTAIN, R. D. Spectral distribution of scattered light in a simple fluid, *Rev. Mod. Phys.*, 1966, **38**, 205-214.
27. KNAPP, H. F. P., GORNALL, W. S. AND STOICHEFF, B. P. Evidence of a fourth component in the Brillouin spectrum of liquid glycerine, *Phys. Rev.*, 1968, **166**, 139-141.
28. KRISHNAN, R. S. Fine structure of the Rayleigh line in amorphous substances, *Nature*, 1950, **165**, 933-934.
29. STRUTT, J. W. (LORD RAYLEIGH, YOUNG) Scattering of light by solid substances, *Proc. R. Soc., Lond.*, 1919, **A95**, 476-479.
30. RAMAN, C. V. The scattering of light in amorphous solids, *J. Opt. Soc. Am.*, 1927, **15**, 185-189.
31. KRISHNAN, R. S. Scattering of light in optical glasses, *Proc. Indian Acad. Sci.*, 1936, **A3**, 211-220.
32. KRISHNAN, R. S. AND RAO, P. V. Molecular aggregation in optical glasses as revealed by light scattering, *Proc. Indian Acad. Sci.*, 1944, **A20**, 109-116.
33. RANK, D. H. AND DOUGLAS, A. E. Light scattering in optical glass, *J. Opt. Soc. Am.*, 1948, **38**, 966-970.
34. DEBYE, P. AND BUECHE, N. M. Scattering by an inhomogeneous solid, *J. Appl. Phys.*, 1949, **20**, 518-525.
35. MAURER, R. D. Light scattering by glasses, *J. Chem. Phys.*, 1956, **25**, 1206-1209.
36. MUELLER, H. On the theory of scattering of light, *Proc. R. Soc. Lond.*, 1938, **A166**, 425-449.
37. TOOL, A. Q. *J. Am. Ceram. Soc.*, 1946, **29**, 240.
38. RITLAND, H. N. *J. Am. Ceram. Soc.*, 1959, **37**, 370.
39. SCHROEDER, J. Light scattering of glass, in *Treatise on materials science and technology*, Vol. 12, 1977, pp. 157-222 (ed. Tomozawa, M. and Doremus, R. H.), Academic Press.
40. KRISHNAN, R. S. Molecular clustering in binary liquid mixtures; Variations with composition and temperature, *Proc. Indian Acad. Sci.*, 1935, **A2**, 221-231; The reciprocity theorem in colloid optics, *Proc. Indian Acad. Sci.*, 1935, **1**, 782-788.
41. KRISHNAN, R. S. Molecular clustering in binary liquid mixtures, *Proc. Indian Acad. Sci.*, 1934, **A1**, 915-927.
42. KRISHNAN, R. S. Dispersion of depolarization of Rayleigh scattering, *Proc. Indian Acad. Sci.*, 1937, **A3**, 566-571, **A5**, 94-107, 305-320, 407-418, 499-509, 551-563, 577-593.
43. KRISHNAN, R. S. The reciprocity theorem in colloid optics and its generalization, *Proc. Indian Acad. Sci.*, 1938, **A7**, 21-34.

44. KRISHNAN, R. S. On the depolarisation of Tyndall scattering in colloids, *Proc. Indian Acad. Sci.*, 1934, **A1**, 717-722.
45. SUBBARAMAIA, D. S. On the depolarization of Tyndall scattering in colloids, *Proc. Indian Acad. Sci.*, 1934, **A1**, 709-716; 1935, **A2**, 358-363.
46. RAMAIAH, K. S. Studies in colloid optics, *Proc. Indian Acad. Sci.*, 1937, **A5**, 128-137, 138-147.
47. WANG, C. H. AND HUANG, Y. Y. Brillouin scattering of light in a cholesteric liquid crystal, *J. Chem. Phys.*, 1975, **62**, 3834-3835.
48. HUANG, Y. Y. AND WANG, C. H. Rayleigh and Brillouin scattering in polybutadiene, *J. Chem. Phys.*, 1974, **61**, 1868-1873.
49. HUANG, Y. Y. AND WANG, C. H. Brillouin, Rayleigh and depolarized Rayleigh scattering studies on polypropylene glycol, *J. Chem. Phys.*, 1975, **62**, 120-126.
50. GANS, R. Zur molekularen schwarmbildung in flüssigkeiten, *Phys. Z.*, 1936, **37**, 19-22; 1937, **38**, 625-627.
51. GROSS, E. Change of wavelength of light due to elastic heat waves at scattering in liquids, *Nature*, 1930, **126**, 201-202.
52. RAMAN, C. V. AND VENKATESWARAN, C. S. Optical observation of the Debye heat waves in crystals, *Nature*, 1938, **142**, 250.
53. CHANDRASEKHARAN, V. Thermal scattering of light in crystals, *Proc. Indian Acad. Sci.*, 1951, **A33**, 183-198.
54. KRISHNAN, R. S. Progress of research on Raman spectroscopy—Indian contributions, *Indian J. Pure Appl. Phys.*, 1988, **26**, 262-267.
55. BHAGAVANTAM, S. The Raman Effect—Its significance for physics and chemistry, *Indian J. Phys.*, 1930, **5**, 237-256.
56. PLACZEK, G. Rayleigh-streuung und Raman-effekt, 1934 in *Handbuch der Radiologie*. Vol. VI, 2, 205-374, ed. E. Marx (An English translation is available : UCRL-Trans- 526(L), United States Atomic Energy Commission, 1962).
57. CARDONA, M. Resonance phenomena, 1982, 19-178, in *Light scattering in solids*, Vol. II, eds M. Cardona and G. Güntherodt, Springer-Verlag.
58. SIRKAR, S. C. On the intensities of the lines in Raman spectra, *Indian J. Phys.*, 1930, **5**, 159-168 and 663-668.
59. SAXENA, B. D. Raman Effect and crystal symmetry, *Proc. Indian Acad. Sci.*, 1940, **A11**, 229-245.
60. BHAGAVANTAM, S. *Scattering of light and the Raman Effect*, 1940, Andhra University Press, Waltair.
61. BHAGAVANTAM, S. AND VENKATARAYUDU, T. *The theory of groups and its applications to physical problems*, 1948, Andhra University Press, Waltair.
62. KRISHNAN, R. S. The Raman spectrum of diamond, *Proc. Indian Acad. Sci.*, 1944, **A19**, 216-223, 298-303.
63. KRISHNAN, R. S. The Raman spectrum of rock-salt, *Proc. R. Soc. Lond.*, 1946, **A187**, 188-196.

64. KRISHNAN, R. S. AND NARAYANAN, P. S. The vibration spectra of the alkali halides, *Proc. Indian Acad. Sci.*, 1948, **A28**, 296-306; *Nature*, 1949, **163**, 570-571.
65. KRISHNAN, R. S. The second order Raman spectrum of diamond, *Proc. Indian Acad. Sci.*, 1946, **A24**, 25-32.
66. BORN, M. AND BRADBURN, M. The theory of the Raman effect in crystals, in particular rock-salt, *Proc. R. Soc. Lond.*, 1948, **A188**, 161-178.
67. BIRMAN, J. Theory of infrared and Raman processes in crystals—Selection rules in diamond and zincblende, *Phys. Rev.*, 1963, **131**, 1489-1496.
68. LOUDON, R. Theory of the first order Raman effect in crystals, *Proc. R. Soc. Lond.*, 1963, **A275**, 218-232.
69. SOLIN, S. A. AND RAMDAS, A. K. Raman spectrum of diamond, *Phys. Rev.*, 1970, **B1**, 1687-1701.
70. COHEN, M. H. AND RUVALDS, J. Two phonon bound states, *Phys. Rev. Lett.*, 1969, **23**, 1378-1381.
71. COCHRAN, W. Crystal stability and theory of ferroelectricity, *Phys. Rev. Lett.*, 1959, **3**, 412-414.
72. RAMAN, C. V. AND NEDUNGADI, T. M. K. The α - β transformation of quartz, *Nature*, 1940, **145**, 147.
73. SCOTT, J. F. Soft-mode spectroscopy—Experimental studies of structural phase transitions, *Rev. Mod. Phys.*, 1974, **46**, 83-128.
74. SAXENA, B. D. Analysis of the Raman and infrared spectra of α -quartz, *Proc. Indian Acad. Sci.*, 1940, **A12**, 93-139.
75. NEDUNGADI, T. M. K. Effect of temperature on the Raman spectrum of quartz, *Proc. Indian Acad. Sci.*, 1940, **A11**, 86-95.
76. SCOTT, J. F. AND PORTO, S. P. S. Longitudinal and transverse optical lattice vibrations in quartz, *Phys. Rev.*, 1967, **161**, 903-910.
77. SCOTT, J. F. Evidence of coupling between one- and two-phonon excitations in quartz, *Phys. Rev. Lett.*, 1968, **21**, 907-910.
78. SCHNEIDER, T., SRINIVASAN, G. AND ENZ, C. P. Phase transitions and soft modes, *Phys. Rev.*, 1972, **A5**, 1528-1536.

Some recent trends in Raman spectroscopy

SUDHANSHU S. JHA

Tata Institute of Fundamental Research, Bombay 400 005, India.

Received on September 21, 1988.

1. Introduction

Even after sixty years since the discovery^{1,2} of the Raman Effect in 1928, Raman spectroscopy continues to be an exciting field of research, covering an increasingly wider spectrum of extremely important problems in physics, chemistry, biology and other branches of science and technology. Ordinarily, this should not be surprising because the frequency-shifted Raman lines, corresponding to inelastic scattering of incident photons by a material medium, directly give the most basic information about the possible excitations in the system. This is obviously very useful in determining the structure and the nature of the material medium at the microscopic level. However, the spontaneous Raman scattering is a very weak second-order electronic process; the scattering cross-section for the Raman process involving vibrational excitations in a typical liquid being only of the order of 10^{-30} cm² per molecule. The signal is extremely small, if the scattering volume is small or the observation time is very short. Moreover, in most cases, while detecting the Raman signal one is faced with a large unwanted fluorescence background arising from the two-step real absorption and emission of photons by impurities, etc., in the sample. In spite of these difficulties, the reason for Raman spectroscopy to remain so popular and extensive is, of course, due to major revolutionary developments which are taking place in optics since the discovery of lasers in the early sixties. These not only relate to the availability of powerful laser sources which can be tuned in a wide range of frequencies and also generated as ultrashort picosecond and femtosecond pulses³, but also to the development of extremely sensitive optical photon-detection systems and multi-channel analysers⁴. They have indeed opened up a vast range of new possibilities in the field.

The main aim of this presentation is not to attempt an exhaustive review of all the recent important developments in the field, but to select an illustrative list of some of these topics for discussing their importance as well as typical results obtained so far. Hopefully, this would bring out, at least partially, the flavour of present trends in research in modern Raman spectroscopy.

In recent years, there has been a greater emphasis on the use of Raman spectroscopy to study the dynamics of a given system and its excitations, instead of just its structural

properties. This is best accomplished by using the so-called time-resolved Raman spectroscopy⁵, with pulsed-laser sources in the appropriate temporal range. This technique will be discussed in some detail in Section 2. In the conventional CW experiment, this information is buried in the shape and the width of the Raman line which, very often, can not be analysed easily for obtaining the relevant dynamical parameters.

The increasing role being played by Resonance Raman Spectroscopy⁶ (RRS) in the investigation of various biological, chemical and other delicate systems like molecules adsorbed on surfaces will be discussed in Section 3. Next, we will consider various types of new studies involving high-vibrational overtone spectroscopy, nonlinear Raman spectroscopies and Fourier-Transform (FT) Raman spectroscopy. Before concluding, we will also mention briefly some recent work on superlattice structures as well as theoretical calculations of Raman intensities for vibrational excitations in molecules.

2. Time-resolved Raman studies

The time-domain optical study of fast dynamical processes at the microscopic level requires ultrashort light pulses, during which the temporal property of the system must not change appreciably. Vibrational energy relaxation in liquids and solids as well as excited-state chemical reactions and energy transfers at the chemical-bond level from one part of a biological molecule to another, represent dynamical processes on the picosecond and subpicosecond time scales. Highly excited nonequilibrium carriers (electrons and holes) in semiconductors can exchange energy among themselves and with lattice phonons on similar ultrashort time scales. In fact, in many cases, the nature of electronic-excited states can change appreciably even in a few femtoseconds. In principle, the time-resolved Raman spectroscopy, in which vibrational (ionic) or electronic excitations of the system are probed by short pulses at different time-delays with respect to the initial time at which the system is prepared in the required state, is an ideal technique for such temporal studies because the intrinsic time of such Raman scattering processes themselves is less than 10^{-15} seconds. In actual practice, the application of the Raman technique for ultrafast time-resolved studies has been slow, mainly because of the difficulties in detecting extremely small Raman signals and in synchronising various steps, including the preparation of the system in the required initial state. However, with the introduction of position-sensitive micro-channel plate photo-multipliers, CCD cameras, powerful monochromators, new pulsing techniques, and various optical data acquisition and processing systems, this situation is changing fast. In the years to come, time-resolved Raman measurements are expected to be a substantial part of the activity in Raman spectroscopy. This is mainly because, in the conventional Raman experiments, one faces serious difficulties in separating various dynamical processes responsible for the line broadening, including inhomogeneous broadening due to a distribution of mode frequencies. Measurements in time-domain directly determine relevant relaxation rates or temporal evolution (whether exponential or not), *e.g.* of mode population, vibrational dephasing, concentration of different transient species, etc.

In the earliest time-resolved Raman experiments⁷, the studies were made mainly of the dynamics of vibrational modes in the electronic ground state of a condensed

medium. Usually, a strong optical pump-pulse was used to prepare the initial state of the system by exciting coherent vibrational modes in liquids like CH_3CCl_3 or phonons in solids like diamond, through the stimulated Raman scattering process or resonant infra-red absorption. A series of weak probe pulses at different time delays was then used to measure the vibrational dephasing time (T_2^*) or the population life-time (T_1), using coherent Raman scattering or the usual incoherent anti-Stokes Raman scattering. In chemistry, it is extremely important to determine the flow of energy between different degrees of freedom in a chemical solution, *i.e.* the complete pathway⁸ for T_1 -relaxation. Molecules in solutions can remain in nonequilibrium (hot) for hundreds of picoseconds. For proper understanding of chemical reactions in solutions, one has to study the vibrational mode frequencies and their dynamics by determining the changes in the potential function for the nuclear motion due to the presence of solvent and other molecules. In general, the investigation of chemical reaction dynamics and the decay of transient species is very important for time-resolved Raman studies in chemistry⁹. Recent incoherent pump-probe Raman experiments, with picosecond-time resolution, have shown that it is indeed possible to obtain such information in a wide range of systems, including pyrrole, haemoglobin, etc. In such a pump-probe technique, the pump beam merely acts to prepare the system far from equilibrium involving *incoherent* superposition of various excitations, and the weak probe beam monitors their population as a function of time *via* Raman scattering from these excitations.

A typical pump-probe set-up is shown in fig. 1, in which both the strong pump and the weak-probe pulses are generated by the same laser beam, but the probe beam is delayed with respect to the pump beam by introducing an additional variable optical length in its path. Ideally, one would like to avoid the detection of the Raman signal arising from the pump beam by choosing the probe frequency quite different than the pump-laser frequency. However, because of technical difficulties, it may not be possible to do so in many situations. In such a case, the real Raman signal from the probe beam is discriminated against the pump scattering by using different polarizations for the pump and probe beams dictated by appropriate polarization selection rules for the excitations¹⁰. The dependence of Raman scattering signal from the probe beam on the delay time t_d at which the probe beam is switched on for a short time t_p , arising from a given excitation mode λ of frequency ω_λ decay constant Γ_λ and occupation number $n_\lambda(t)$, is approximately determined by the temporal functions

$$G_{\text{Stokes}}^\lambda(t = t_d + t_p) = \left| \int_0^{t_p} d\tau e^{-i(\omega_S - \omega_I - \omega_\lambda - i\Gamma_\lambda)\tau} [n_\lambda(t_d + t_p - \tau) + 1] \right|^2 \quad (1)$$

$$G_{\text{A Stokes}}^\lambda(t = t_d + t_p) = \left| \int_0^{t_p} d\tau e^{-i(\omega_S - \omega_I - \omega_\lambda - i\Gamma_\lambda)\tau} [n_\lambda(t_d + t_p - \tau)] \right|^2 \quad (2)$$

where ω_S and ω_I are scattered and incident frequencies, respectively^{11,12}. If one assumes that during the short-probe pulsewidth, the system properties including $n_\lambda(t)$ do not change appreciably, the above expressions lead to the signals proportional to $n_\lambda(t_d) + 1$ and $n_\lambda(t_d)$, with Raman lines of width π/t_p at the frequencies $\omega_S = \omega_I \mp \omega_\lambda$, respectively, for $1/\Gamma_\lambda$ large compared to the pulsewidth t_p . This implies that for spectral resolution of

microchannel plate photomultiplier/CCD

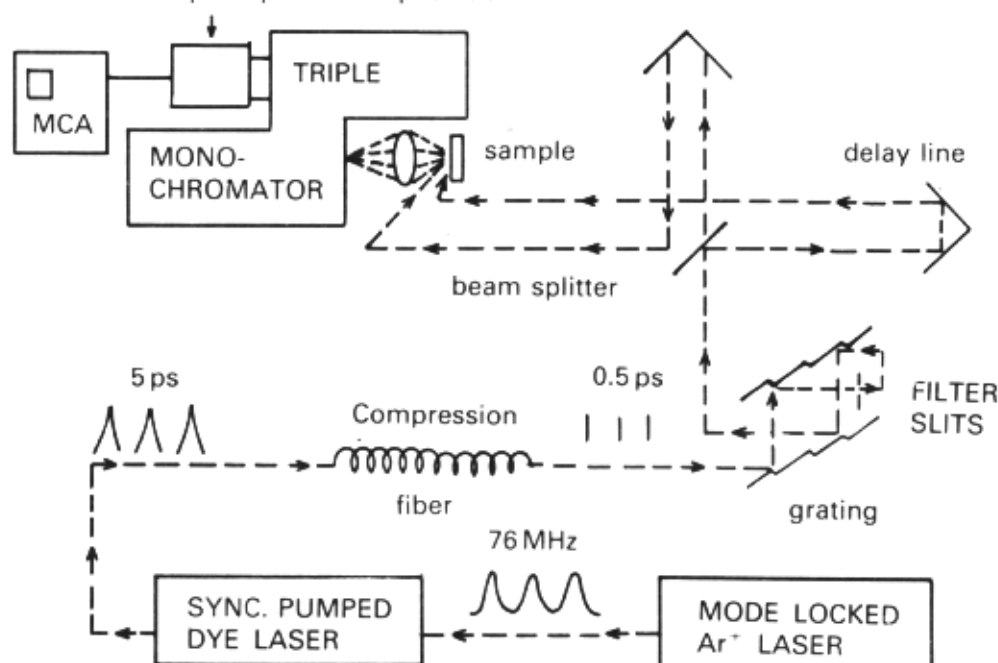


FIG. 1. Typical pump-probe Raman scheme.

at least 100 cm^{-1} , one can not use pulses shorter than 200 femtoseconds¹². For shorter pulses, one can only monitor much higher frequency vibrational modes or electronic excitations, because of the uncertainty principle.

Recently, dynamics of nonequilibrium carriers and LO-phonons have been studied^{13,14} in several polar semiconductors like GaAs, InAs, $\text{Al}_x\text{Ga}_{1-x}\text{As}$ and $\text{In}_x\text{Ga}_{1-x}\text{As}$, using subpicosecond pump-probe Raman technique. A very short laser pulse, with photon energy above the band gap of the intrinsic semiconductor, pumps electrons from its valence bands to the conduction band with carrier densities in the range of 10^{16} to 10^{18} cm^{-3} , depending on the total pump-laser energy. Because of the strong Fröhlich interaction of carriers with LO-phonons, electrons and holes relax towards band extrema by emitting long-wavelength LO-phonons on a time scale of 150 to 200 femtoseconds. Since the lifetime of the generated LO-phonons is much longer (several picoseconds), their occupation number first increases from its equilibrium value as a function of time t_d , before decreasing towards the equilibrium value. The Raman signal of the probe beam, either on the anti-Stokes side or on the Stokes side, directly monitors this temporal evolution as a function of the time delay t_d . The initial rising slope gives the electron-LO-phonon scattering time (about 160 femtoseconds in GaAs) and the later fall determines the LO-phonon decay time, for different lattice temperatures of the sample. Because of the current interest in fabricating fast electronic devices, these studies are also being extended to quantum-well and superlattice structures of GaAs and AlAs.

3. Resonance Raman Spectroscopy (RRS)

The advent of powerful lasers in the early sixties, allowed increased source intensity with an extremely narrow spread of incident frequencies, and the resulting increase in signals for the spontaneous Raman scattering. However, this ease in detection was not very useful for investigating many delicate biological and chemical systems or for studying processes at solid surfaces involving very small scattering volumes. In such systems, one faces severe limitations in increasing the incident laser intensity because that can heat and alter the nature of the system itself, which is under study. On the other hand, with easy availability of tunable lasers in the late sixties and early seventies, it was realised that one could enhance the basic Raman scattering process itself by several orders of magnitude by tuning the incident laser frequency close to one of the electronic intermediate states of the medium under study. Since Raman transition polarizability is a second-order perturbation process involving the interaction of the electrons in the system with the incident photons (ω_i) and the scattered photon (ω_s), the cross section has also a resonance structure when ω_i or ω_s is close to an electronic intermediate state of the system. The essential point is that in the so-called Resonance Raman Spectroscopy (RRS), the signal can be increased by a factor of approximately $(\hbar\omega_i)^2/(\hbar\Gamma_n)^2$, where $\hbar\Gamma_n$ is the transition width of the intermediate electronic state n .

The extension of RRS up to the ultraviolet (UV) region of the incident frequency has allowed the study of many important biological molecules and processes. Prosthetic groups such as heme, flavin, retinal and metal-ion centres, and aromatic chromophores in complex environments have been recently investigated using visible and UV excitations¹⁵. Apart from other studies of nucleic acid structures, lipids and related systems, new studies of benzene, benzene derivatives, ammonia, oxygen, etc., have also been made using far UV-RRS to determine changes in the excited-state geometry and highly excited vibrational levels of the ground electronic state¹⁶. By pulsing the incident laser, it has also been possible to couple RRS with the time-resolved studies of protein dynamics. In RRS, partial depolarization of the resonance Raman signal from molecular vibrations is present if the molecules could rotate during the time interval between the absorption and emission steps. In fact, the measurement of the depolarization ratios in RRS can give very important data on fast collisional processes in liquids, because the efficiency of RRS depends essentially on the dephasing time of the intermediate electronic state. The excited-state rotation and collisions with solvent molecules give a value of the dephasing time of the order of 10^{-13} seconds, which leads to a partial depolarization of RRS.

The study of adsorption and reaction dynamics of a very small number of layers of molecules on the surfaces of metals and semiconductors has become possible in recent years, because of the development of the so-called Surface-Enhanced Raman Spectroscopy (SERS) and the new highly sensitive optical-detection techniques. For many molecules adsorbed on metals like Ag, Au, Pt, Al, etc., there is a large enhancement of Raman cross-sections for various vibrational modes of the molecules¹⁷, due to resonance of the incident and/or scattered frequencies with the electromagnetic surface-plasmon-polariton modes of the medium or with the charge-transfer band of the surface complex formed by the molecule and the solid substrate. SERS has been used to study many

important processes at electrodes and in biological molecules. Of course, new optical-detection techniques have now allowed observation of very weak Raman signals from adsorbed molecules, even without any apparent resonance enhancement.

4. Vibrational overtone, FT Raman, and nonlinear Raman spectroscopies

In polyatomic molecules, anharmonicity of nuclear motion on a potential energy hypersurface becomes increasingly important with increasing amplitude of vibration. In fact, small amplitude normal-mode picture collapses as the amplitude of vibration approaches bond dissociation. Because of the lowering of the restoring force at the outer turning points, the separation between vibrational levels in a diatomic molecule decreases with increase in vibrational energy. In general, bond-stretching vibrations decouple from other molecular motions and get localized, if we increase vibrational energy in that bond. The measurement of overtone vibrational frequencies in the region of very high vibrational energies gives essential information in constructing the complete potential energy hypersurface which is important in understanding the mechanism of any chemical reaction involving such molecules. With increased sensitivity of optical detectors, it is expected that the observation of Raman scattering from high vibrational overtones will complement similar studies using infrared spectroscopy.

The use of Raman scattering technique for analytical purposes has always been slow because of the need to eliminate background fluorescence signal which can sometimes be much stronger than the Raman signal. This problem is more severe, if one is not analysing samples of single-component compounds. With the development of Fourier-transform (FT) infrared spectroscopy in recent years, it is now possible to obtain FT Raman spectra with almost no fluorescence background. When samples are irradiated in the near infrared, there is only weak absorption due to excitations of overtones and combinations of fundamental vibrations, and fluorescence is almost absent with the usual energy of infrared laser being used in Raman experiments. Instead of the dispersive elements used in detecting optical signals in the conventional Raman spectroscopy, a Michelson interferometer, or other interferometric method is used to detect signals in FT-Raman spectroscopy. This results in very high resolution and allows measurement of even very small-frequency shifts, with the possibility of a better accuracy in absolute frequency measurements. The optimization of various systems in FT-Raman instrumentation is still continuing, but its application to various interesting systems in future seems very promising.

Development of intense tunable lasers with high spatial and temporal coherence has also allowed the use of nonlinear Raman spectroscopies to solve problems which can not be tackled otherwise. These arise because of the third-order term involving $\chi^{(3)}\bar{E}\bar{E}\bar{E}$ in the induced-polarization \bar{P} of the medium. When incident radiation fields at frequencies ω_1 and ω_2 (let $\omega_1 > \omega_2$) are present in coincidence in space and time in the medium, such that $\omega_1 - \omega_2$ is equal to the frequency ω_0 of a Raman-active excitation, because of the $\chi_R^{(3)}(\omega_1, -\omega_2, \omega_1)$ term one can study the gain in the amplitude of the wave at the lower frequency ω_2 (Raman-gain spectroscopy), or a loss at the higher-frequency wave at ω_1 (Inverse Raman spectroscopy), or the growth of the amplitude of a new wave at $2\omega_1 - \omega_2$

(CARS). Whereas the changes in intensities of the waves at ω_1 and ω_2 are related to the imaginary part $\chi_R^{(3)*}$, the CARS intensity is related to $|\chi_{\text{CARS}}^{(3)}|^2 = |\chi_R^{(3)*} + \chi_{\text{NR}}|^2 + |\chi_R^{(3)*}|^2$. Here, the signals in these nonlinear spectroscopies are background free because of the special need for temporal and spatial coincidence of beams in these processes. However, due to the nonresonant contribution χ_{NR} in CARS, there are distortions in the line shapes in CARS as opposed to, e.g., Raman-gain (amplification) spectroscopy. Since gases can withstand very high power needed in these spectroscopies, they have been applied very successfully in recent years for very high-resolution Raman studies in such systems. Using picosecond-pulsed lasers, Raman amplification technique can also be used in the condensed phase, e.g., in a single crystal of ion-exchange resin which is otherwise extremely fluorescent. In high-order processes beyond $\chi^{(3)}$, one can generate new waves when $\omega_1 - \omega_2$ is equal to a subharmonic of the active Raman mode ω_0 . For example, with $\chi_R^{(5)}$ ($\omega_1, -\omega_2, \omega_1, -\omega_2, \omega_1$), one creates waves²¹ at $\omega_1 - \omega_2 = \omega_0/2$. However, these signals may not necessarily contain any more information than that obtained in the lower-order nonlinear spectroscopies.

5. Concluding remarks

Before concluding, let us emphasize here that in this article we have touched upon only a very small sub-set of present interesting topics in Raman spectroscopy. Among many other important investigations like high-pressure Raman experiments, etc., we have not said anything about the beautiful Raman studies of acoustic phonons in periodic semiconductor lattices as well as non-periodic (Fibonacci quasi-periodic, random, etc.) lattices. These structures consist of sequences of two building blocks of GaAs and AlAs layers of thickness of the order of 20 to 40 Å or so. Because of zone-folding in the \vec{q} -space, in the direction of the superlattice structure, acoustic phonons have many different sets of longitudinal and transverse branches, starting from $\vec{q} = 0$, with a much shorter first Brillouin-zone in the \vec{q} -space. Long-wavelength ($\vec{q} \rightarrow 0$), finite-frequency modes can then be observed *via* Raman scattering. This provides extremely useful information about the structural and elastic properties of these layered materials²². In a sense, acoustic-Raman scattering studies in a periodic superlattice can approximately map the acoustic phonon dispersion relations of the original bulk materials up to the large original Brillouin-zone in the \vec{q} -space, in the direction of the superlattice structure.

Substantial progress has also been made in calculating Raman-scattering intensities for vibrational excitations in various molecules, from first principles. Since the computation of absolute Raman cross-sections has always been a troublesome theoretical problem, one is often content with only relative comparisons of experimental results with theoretical predictions. However, recent *ab initio* calculations²³ of the polarizability derivatives in molecules like H₂O, etc., *via* direct computation of electronic energy derivatives, have been quite promising.

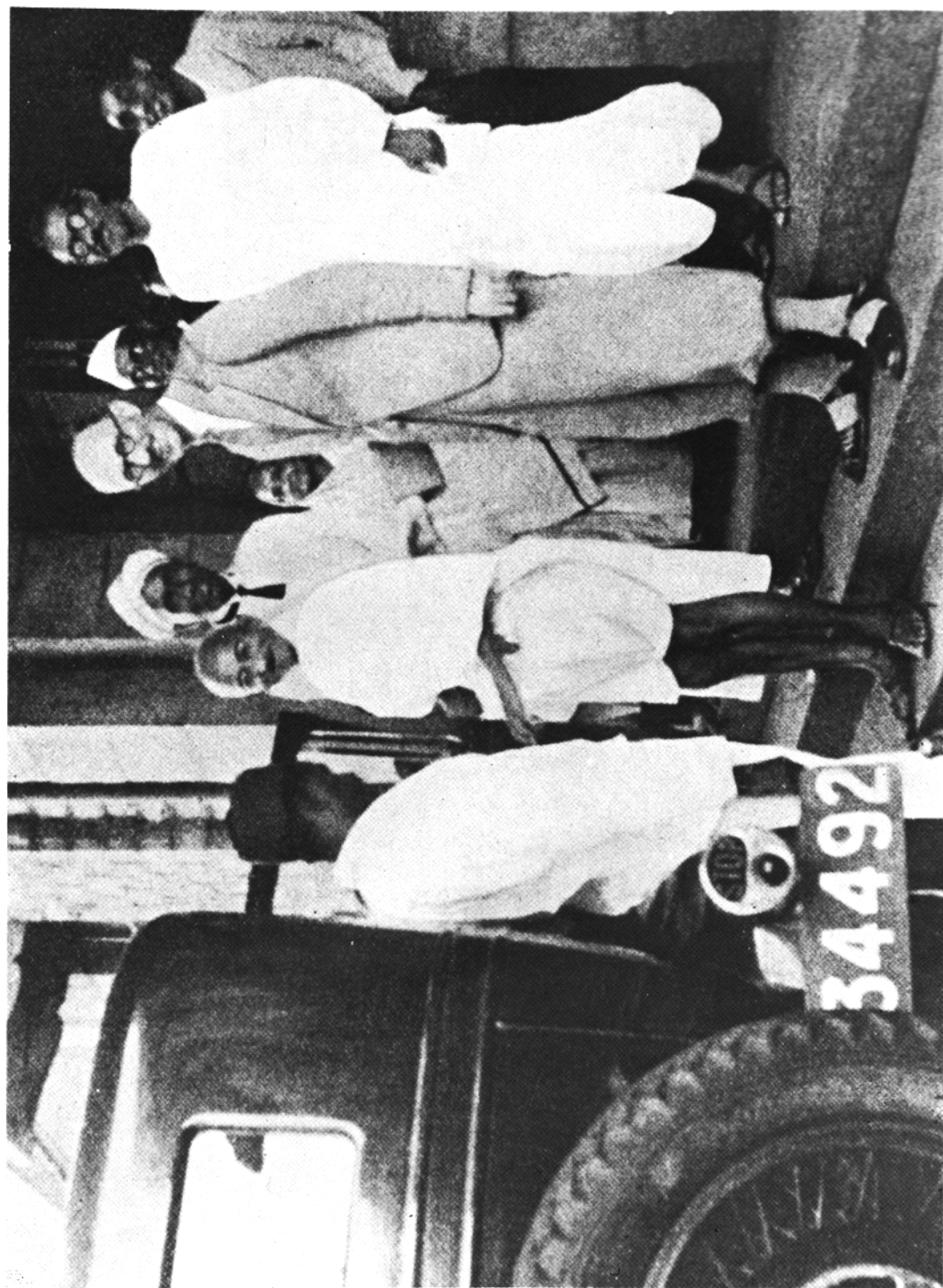
The present activity in the field of Raman spectroscopy is quite vast and very extensive. Since it covers many diverse disciplines in science, it has been difficult to do justice to various exciting developments taking place in the field, in an article like this. The vitality of the field is proved by the exciting proceedings of biennial international confe-

rences on Raman spectroscopy, and by the increasing number of interesting papers being published in the field in a large number of research journals. With the rapid growth of sophistication and sensitivity in optical detection and data-processing techniques, and the progress made in controlling and generating tunable optical sources which can be pulsed to the level of a few femtoseconds, different forms of Raman spectroscopy are expected to remain in the limelight for decades to come.

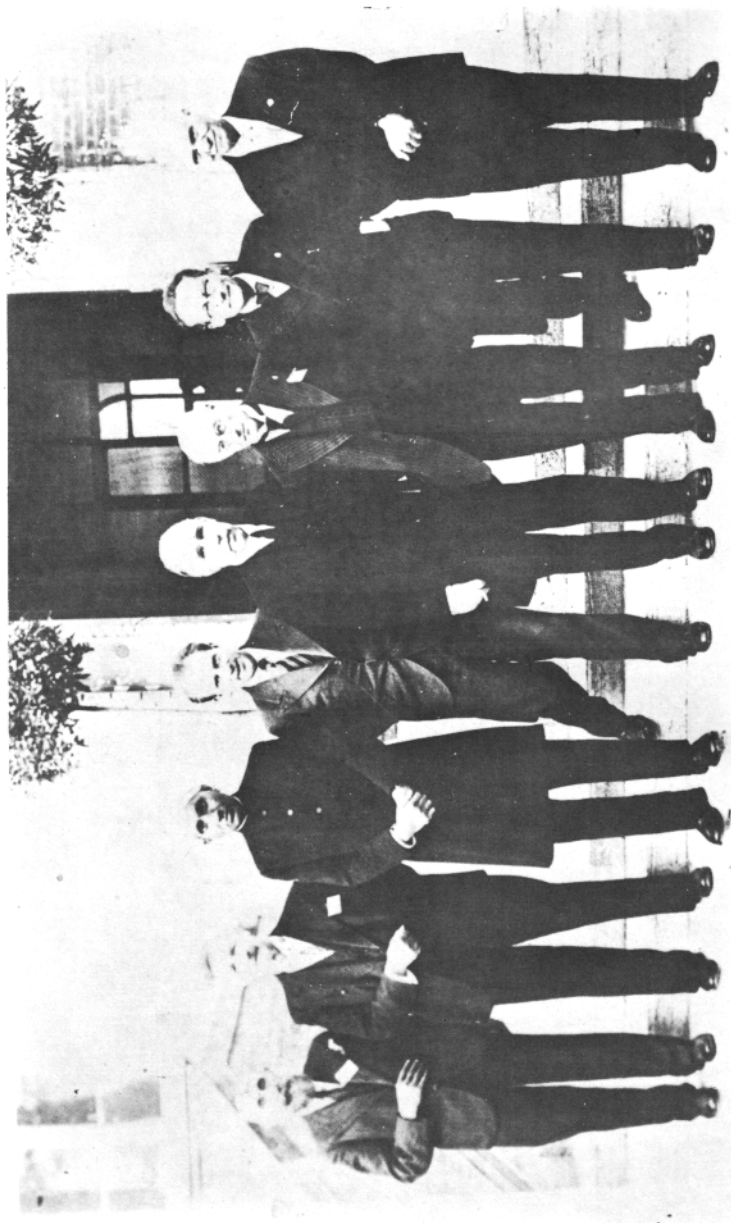
References

1. RAMAN, C. V. AND KRISHNAN, K. S. *Nature (Lond.)*, 1928, **121**, 501.
2. RAMAN, C. V. *Indian J. Phys.*, 1928, **2**, 387.
3. IPPEN, E. P. AND SHANK, C. V. In *Ultrashort light pulses*, 1977 and 1984, Topics in Applied Physics, Vol. 18, ed. S. L. Shapiro, Springer-Verlag, Heidelberg.
4. CHANG, R. A. AND LONG, M. B. In *Light scattering in solids II*, 1982, Topics in Applied Physics, Vol. 50, ed. M. Cardona and G. Guntherodt, Springer-Verlag, Heidelberg.
5. see, e.g., *Time-resolved vibrational spectroscopy*, 1985, ed. A. Laubereau and M. Stockburger, Springer-Verlag, Heidelberg.
6. HUDSON, B. *Spectroscopy*, 1986, **1**, 22.
7. KAISER, W. AND LAUBEREAU, A. *Rev. Mod. Phys.*, 1978, **50**, 607.
8. VELSKO, S. AND HOCKSTRASSER, R. M. *J. Phys. Chem.*, 1985, **89**, 2240.
9. HAMAGUCHI, H. In *Vibrational spectra and structure*, Vol. 16, 1987, ed. J. Durig, Elsevier, New York.
10. KASH, J. A., TSANG, J. C. AND HVAM, J. M. *Phys. Rev. Lett.*, 1985, **54**, 2151.
11. JHA, S. S. *Indian J. Pure Appl. Phys.*, 1988, **26**, 192.
12. JHA, S. S., KASH, J. A. AND TSANG, J. C. *Phys. Rev.*, 1986, **B34**, 5498.
13. TSANG, J. C., KASH, J. A. AND JHA, S. S. *Physica*, 1985, **B134**, 184.
14. KASH, J. A., JHA, S. S. AND TSANG, J. C. *Phys. Rev. Lett.*, 1987, **58**, 1869; *ibid.*, 1988, **60**, 864.
15. see, e.g., *Spectroscopy of biological molecules*, Vol. 13, 1984, ed. R. J. H. Clark and R. E. Hester, Wiley, Chichester.
16. HUDSON, B. AND SENSION, R. J. In *Vibrational spectra and structure*, Vol. 17, 1988, ed. J. R. Durig, Elsevier, New York.
17. a. MOSKOVITS, M. *Rev. Mod. Phys.*, 1985, **57**, 783.
b. JHA, S. S. *Surf. Sci.*, 1985, **158**, 190.
c. OTTO, A. *Surf. Sci.*, 1987, **188**, 519.

18. CHASE, B. *J. Am. Chem. Soc.*, 1986, **108**, 7485.
19. CHASE, B. *Anal. Chem.*, 1987, **59**, 881A.
20. NIBLER, J. W. AND PUBANZ, G. A. In *Advances in nonlinear spectroscopy*, Vol. 15, 1984, ed. R. J. H. Clark and R. E. Hester, p. 1, Wiley, Chichester.
21. TARAN, J. P. AND JONES, W. J. In *Proc. XI Int. Cong. on Raman Spectroscopy*, 1988, ed. R. J. H. Clark and D. A. Long, p. 31, Wiley, Chichester; see also, *ibid*, p. 35.
22. MERLIN, R., BAJEMA, K., NAGLE, J. AND PLOOG, K. *J. Phys.*, (Paris), 1987, **48**, C5-503.
23. AMOS, R. D. *Adv. Chem. Phys.*, 1987, **69**, 241.



Professor Raman with Mahatma Gandhi at the Institute (1936).

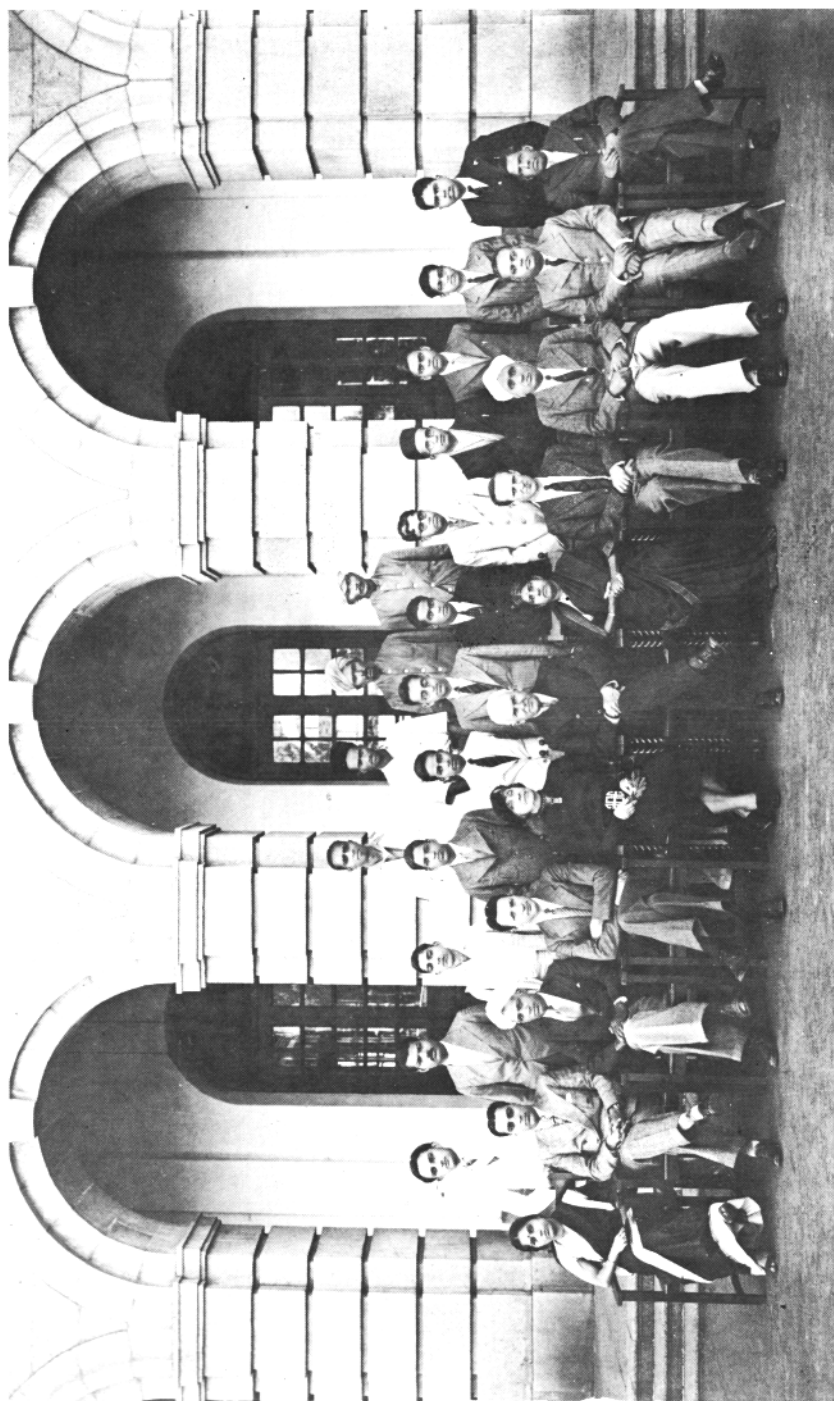


Courtesy: T. M. K. Nedungadi

Professor Raman (third from left) seen with a group of distinguished scientists, among whom may be seen W. Heisenberg, Niels Bohr and E. Schroedinger (fourth, fifth and seventh from left).



A 1936 photograph showing Professor and Lady Raman with Max and Hedi Born (third to sixth from left, front row). Also seen in the picture are C. S. Venkateswaran, N. S. Nagendra Nath, (first and seventh from left, front row) R. Ananthakrishnan, B. V. R. Rao, (second and sixth from left second row) and R. S. Krishnan (third from right, last row).



Courtesy: B. V. R. Rao.

A 1940 photograph showing Professor and Lady Raman with R. A. Millikan and Mrs. Millikan (fifth and sixth from left, front row). Also seen in the picture are H. J. Bhabha, K. R. Ramanathan, H. V. Neher, W. H. Pickering (second, third, fourth and eighth from left, front row), Vikram A. Sarabhai and T. M. K. Nedungadi (first and fourth from left, second row).



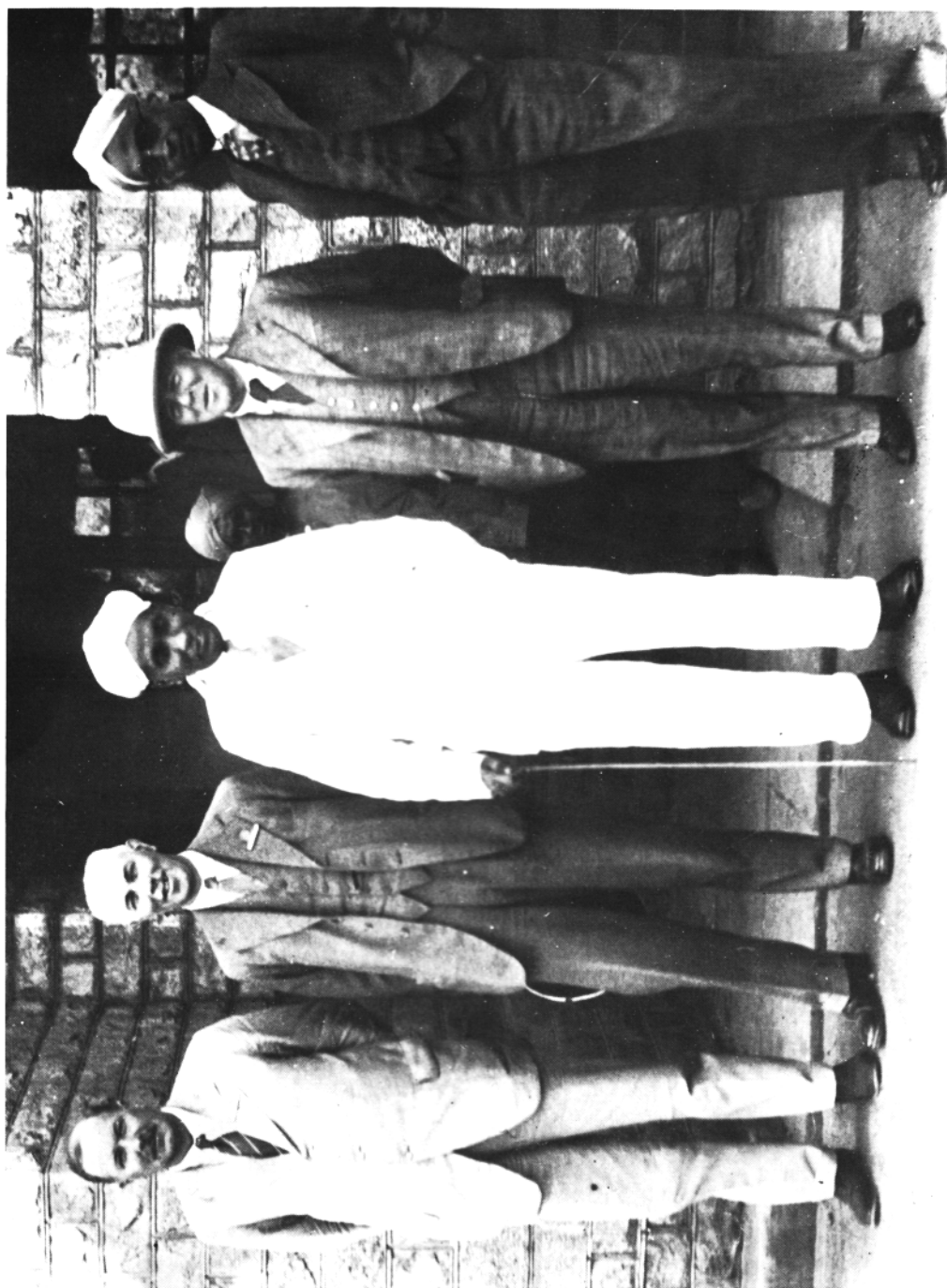
Professor Raman with visitors in his lab.

Courtesy: S. Ramaseshan



Courtesy: S. Ramaseshan

Professor Raman with some colleagues and associates, among whom can be seen K. S. Krishnan (first from left, front row), T. R. Seshadri, K. Ramaiiah and S. Bhagavantam (third, second and first from right, third row).



Courtesy: T. M. K. Nedungadi

Professor Raman with K. Aston (to his immediate right), O. W. Richardson and B. Venkatesachar (to his immediate and far left).



Professor Raman with Pandit Nehru.

The resonance Raman spectrum of I_2 in solution

HERBERT L. STRAUSS

Department of Chemistry, University of California, Berkeley, California 94720, U.S.A.

Received on August 26, 1988.

Abstract

An extensive set of resonance excitation profiles and the corresponding depolarization dispersion profiles of the vibrational bands of iodine in solution were determined. The results of the experiments are compared to the results of detailed calculations. The calculations are based on the gas phase potentials of iodine. Overall agreement is good for the noninteracting solvents considered here. However, there are a number of discrepancies, which suggest that higher iodine states — perhaps charge transfer states involving the solvent — contribute to the Raman cross section in the visible region of the spectrum. A number of other small effects, such as rotation of iodine in the excited states, also contribute.

Key words: Resonance excitation profiles, resonance Raman spectrum, iodine properties.

One day in the Spring of 1969, I knocked at the door of C. V. Raman's residence in Bangalore. I had come despite the warnings of my friends at the I.I.Sc. and the forbidding sign that Raman had erected beside his front gate. However, the Ramans greeted me with enthusiasm and Raman showed me his latest work, while Mrs. Raman made tea. We spent a very enjoyable few hours together. Raman was eager to discuss both his recent work and that of years past. He continued to relish his older work and restate his sometimes controversial positions from long ago. A month later I met with Professor Charles Coulson in Oxford. When I recounted some of Raman's conversation, he said, "That's just what he said to me at a meeting in 1937!" One of Raman's lifelong interests was the color of things, especially his prized flowers. It is with this in mind that I discuss in this paper the effect of changing the color of the excitation on the Raman Effect of the well-known colored solutions of I_2 .

Two observations led to this investigation. The first is the profound changes in the relative intensity of the iodine fundamental and its overtones as the frequency of the exciting laser is changed throughout the visible band. The second and more unusual observation is that the Raman bands apparently shift as the color of the laser is changed (fig. 1)¹.

The visible spectrum of I_2 is one of the spectra most thoroughly studied by molecular spectroscopy. The electronic states of I_2 have been particularly well characterized in the spectral region that contributes to the visible absorption and fluorescence spectra²⁻⁵. The potential energy curves for the states that contribute to the visible absorption are

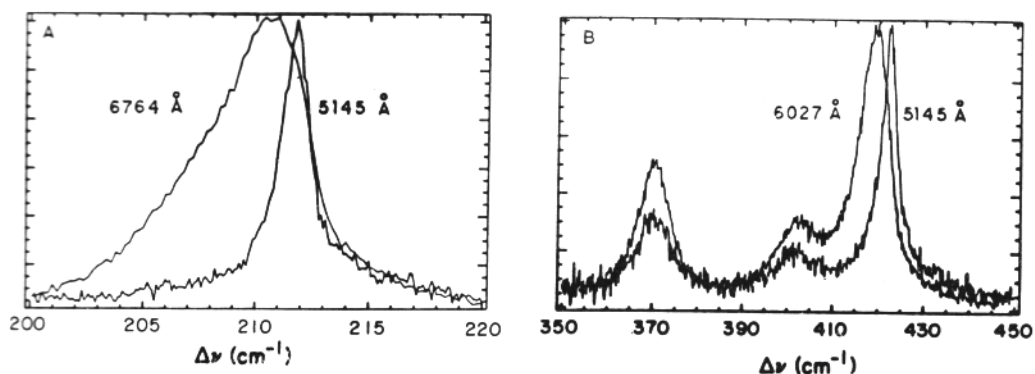


FIG. 1. High-resolution Raman spectra of the fundamental (A) and first overtone (B) of I_2 in *n*-hexane. Each spectrum is labeled with the laser excitation wavelength. The changes that occur in the band shapes and positions are due to the relative resonance enhancements of the hot bands. The frequency scale for each spectrum of the overtone was calibrated relative to the *n*-hexane band at 370 cm^{-1} . The band at 402 cm^{-1} is another solvent band.

shown in fig. 2⁶. The low-resolution spectrum of I_2 vapor is shown in fig. 3. The total absorption band is composed of three parts. About 5% of the total absorption is due to the $A \leftarrow X$ transition, which gives rise to the weak low-frequency wing. At the high-

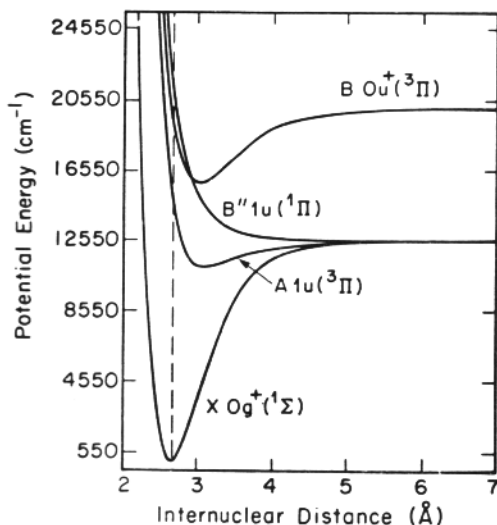


FIG. 2. Potential energy curves for the electronic states of I_2 that contribute to the visible absorption spectrum. The dashed line at 2.67 Å represents the equilibrium internuclear distance for ground state I_2 (redrawn from ref. 6).

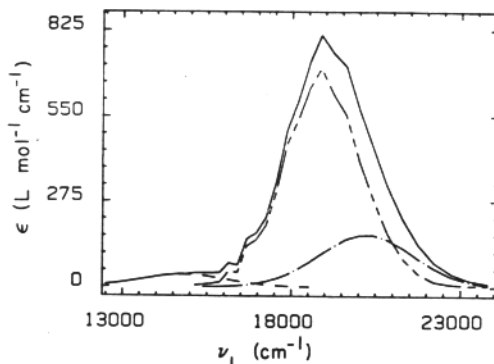


FIG. 3. The low-resolution absorption spectrum of I_2 vapor. The solid line is the total absorption, the contribution of the $A \leftarrow X$ transition is represented by the dashed line, the contribution of the $B'' \leftarrow X$ transition is represented by the dot-dashed line, and the contribution of the $B \leftarrow X$ transition is represented by the dash-dashed line. Note that the difference between the $A \leftarrow X$ and the total absorption is negligible below $14,500\text{ cm}^{-1}$. The total spectrum and the breakdown into contributing transitions are plotted from the table of values in ref. 2. The bumpiness in the $B \leftarrow X$ spectrum is the result of residual vibrational structure.

frequency side the B'' ← X transition appears, and this accounts for 22% of the absorption. The main B ← X transition accounts for 73% of the absorption.

The properties of iodine in solution have been of interest to scientists for at least a century⁷. Most spectral studies of iodine in solution have dealt with the charge-transfer interactions between I₂ and the solvent⁸. Recently, much attention has been focused on the effect of solvents on the predissociation of I₂ and subsequent recombination of the I atoms^{9,10}.

Theory predicts that, in the resonance region, the Raman spectrum of I₂ will depend on the frequency of the laser and on the interaction of the solvent with the excited states of the spectroscopically active molecule. The differential cross section for the Raman cross-section of a randomly oriented gas phase molecule is given by¹¹⁻¹³

$$\frac{d\sigma}{d\Omega} = \left(\frac{4\pi^2}{hc}\right)^2 \nu_S^3 \nu_L \left| \sum_{\rho\sigma} l_{S\rho} \alpha_{\rho\sigma}(\nu_L, I, F) l_{\sigma L} \right|^2, \quad (1)$$

where the elements of the polarizability tensor, $\alpha_{\rho\sigma}$, are given by

$$\alpha_{\sigma\rho}(\nu_L, I, F) = \sum_E \frac{\langle F | \mu \cdot \epsilon_\rho^* | E \rangle \langle E | \mu \cdot \epsilon_\sigma | I \rangle}{\nu_E - \nu_I - \nu_L - i\Gamma_E}. \quad (2)$$

Here I and F are the initial and final states of the molecule and the summation over E is over all the states of the molecule. ν_S , ν_L , ν_E and ν_I are the energies (in cm⁻¹) of the scattered light, the incident laser, the intermediate state E and the initial state I , respectively. Γ is the width of the intermediate state. The polarization vectors of the scattered photons, ϵ_ρ and the incident photon, ϵ_σ , are referred to the molecular-fixed frame. The direction cosines $l_{S\rho}$ and $l_{\sigma L}$ convert this frame to the laboratory frame of reference. A number of steps are required to convert this formula to usable form. The averages over the direction cosine elements are taken and lead to expressions involving specific components of the α -tensor. The dipole matrix elements such as $\langle F | \mu | I \rangle$ are separated into electronic and vibrational parts by invoking the Born-Oppenheimer approximation. Finally, the appropriate index of refraction corrections for the presence of the solvent are made.

The results of the calculations are formulas for the total differential cross-section and for the polarization ratio in terms of the components of the polarizability. For I₂ there are two such components, $\alpha_{\gamma\gamma}$ where γ is the molecular axis, and $\alpha_{\beta\beta}$ where β is an axis perpendicular to γ . For the B ← X transition the only non-zero terms are in $\alpha_{\gamma\gamma}$, and for the A ← X and B'' ← X transitions only the $\alpha_{\beta\beta}$ survive. As a consequence, the depolarization ratio would be 1/8 if only the A and B'' states contribute to the Raman cross-section and 1/3 if only the B state contributes.

We have made four types of measurements and compared the results to detailed calculations¹³⁻¹⁶. In doing this, we had two goals in mind. The first is to provide a comprehensive test of the theory of the resonance effect and to resolve various contradictions in

the literature. The second is to determine the properties of the excited states of I_2 in solution. As we shall see, the information available from resonance Raman spectroscopy is complementary to that from absorption spectroscopy.

The four types of measurements are: (1) The resonance excitation profile, REP; that is, the change of intensity of the various I_2 Raman bands as a function of the frequency of the exciting laser. This measurement was done in *n*-hexane, a rather non-interacting solvent. (2) The depolarization dispersion profiles which we call DDPs; that is, the variation of the depolarization ratio *versus* frequency of the exciting laser. (3) The REPs in other non-interacting solvents. (4) The variation of the band shapes of the I_2 Raman spectrum with laser frequency.

It is worthwhile to digress to consider the theory of the resonance Raman Effect further. In eqn (2), the Γ in the denominator is the lifetime of the excited state for a gas phase molecule. For a molecule in condensed phase, the correctness of using Γ to account for interactions with the surroundings is not so clear. We followed the formulation of Mukamel¹⁷ which shows that Γ is $1/T_2$ for the intermediate state. Mukamel's

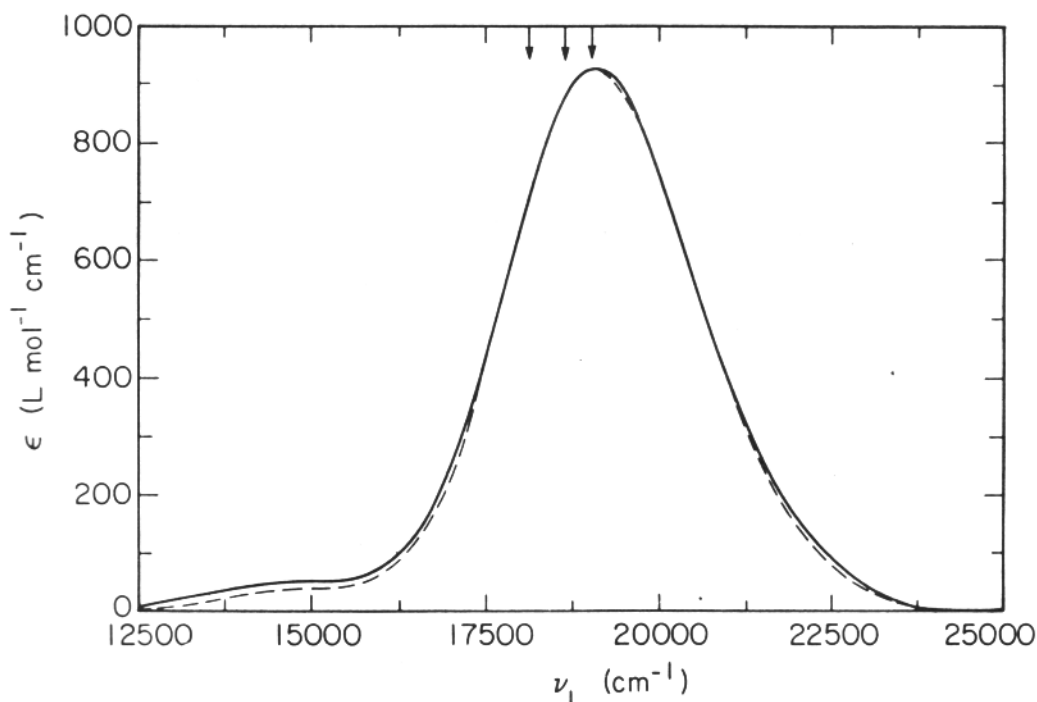


FIG. 4. The experimental (dashed line) and calculated (solid line) visible absorption spectrum of I_2 in *n*-hexane. The anharmonic ground state, discussed in the text, was used for all calculations of I_2 in *n*-hexane. The calculation parameters are: $\Gamma = 20 \text{ cm}^{-1}$; θ , the inhomogeneous width, $= 400 \text{ cm}^{-1}$; and $T = 300 \text{ K}$. The calculated spectrum is fairly insensitive to $\Gamma < 100 \text{ cm}^{-1}$. The intensity of the B state absorption was matched using $L^2 = 1.75$ as a solution correction factor. The width of the spectrum was matched by adjusting θ . The calculated spectrum fits less accurately in the high and low frequency wings where the A and B' states dominate.

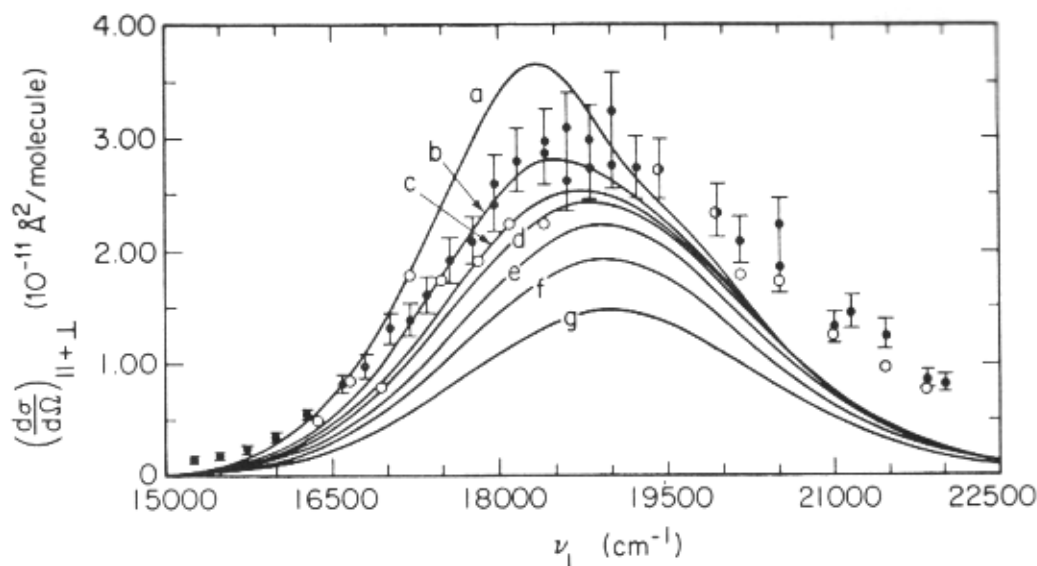


FIG. 5. Calculated and experimental REPs for the I₂ fundamental in *n*-hexane plotted on an absolute scale. The data points with error bars are our experimental values (the error bars shown are $\pm 10\%$). The results of repeated experiments are shown as multiple data points. The open circles represent data points from Rousseau *et al.*¹⁹. These points were scaled to our value of the absolute cross section at 5145 Å. The homogeneous linewidths, or damping factors, are as follows: $\Gamma =$ (a) 10 cm⁻¹, (b) 15 cm⁻¹, (c) 20 cm⁻¹, (d) 25 cm⁻¹, (e) 50 cm⁻¹, (f) 100 cm⁻¹, and (g) 200 cm⁻¹. The inhomogeneous linewidth and the solvent effect on the transition strength are both determined by the absorption spectrum.

formulas contain separate terms for the resonance Raman scattering and the resonance fluorescence. The latter is very broad and we ignore it in what follows.

The total resonance Raman intensity varies with Γ in stark contrast to total intensity of an absorption spectrum, which is of course invariant to the width of the states. Thus a measurement of the absolute intensity of the Raman Effect determines Γ , provided we have a model of the vibronic states that allows us to calculate the matrix elements of eqn (2). To determine these, we assume that the electronic states of I₂ are the same in hexane as they are in the gas phase. However, we do modify the ground state vibrational states in hexane and the other solvents we have used to match the observed anharmonicity for each one¹⁸. Our calculations match the observed absorption spectrum well, as shown in fig. 4¹⁹.

We take up the Raman Effect experimental results in order. Figure 5 shows the resonance excitation profile for the I₂ fundamental. Also on the figure are the results of calculations which we discuss in a moment. Figure 6 shows the data for the first and second overtones of I₂. In applying the gas phase electronic data to the solution spectra, we chose a value of Γ to give the best fit. The best choice for Γ is about 20 cm⁻¹ and gives an excellent overall fit, but there are a number of discrepancies. Note that the experimental points are higher than calculated ones at the high-frequency side of the REP of the fundamental and at the peak of the REP of the first overtone.

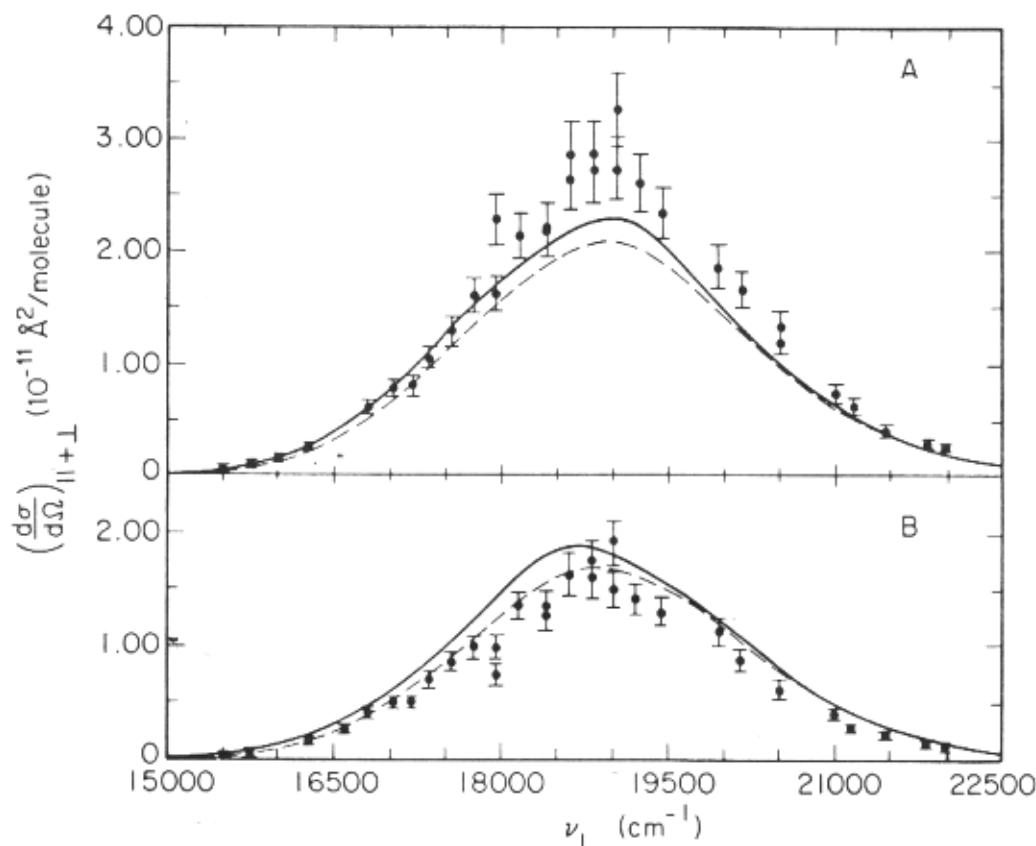


FIG. 6. Calculated and experimental REPs for the I_2 first (A) and second (B) overtones in *n*-hexane. The error bars on the experimental points are $\pm 10\%$ as in fig. 5. The parameters for the calculations are $\Gamma = 20 \text{ cm}^{-1}$ (dashed lines) and $\Gamma = 15 \text{ cm}^{-1}$ (solid lines). Note that Γ is the only adjustable parameter and the ordinate scale is absolute.

To obtain a better fit, we consider the depolarization dispersion profiles and also vary the calculations systematically to test various effects of the solution excited states. Figure 7 shows the new calculations with the same data for the REP of the fundamental. Also shown is the DDP of the fundamental. Near the center of the absorption bands the DDP is almost $1/3$, the value for the B state alone, as expected. At the low- and high-frequency wings of the band the DDP changes away from $1/3$ as the A, B', and other degenerate states participate. We show similar information for the first overtone in fig. 8. In an attempt to resolve the discrepancies mentioned, we included the contribution from the D state in the calculation. The D state is at much higher energy in the isolated I_2 molecule — at about $54,000 \text{ cm}^{-1}$. It contributes to the Raman spectrum near the I_2 visible absorption band through the B-D cross term that appears in the expression for the polarizability squared. As seen in figs 7 and 8, the fundamental REP is still in disagreement as before, but the overtone REP is in rather better agreement. This is partly due to a recalibration of the absolute intensity, which is based on comparison with

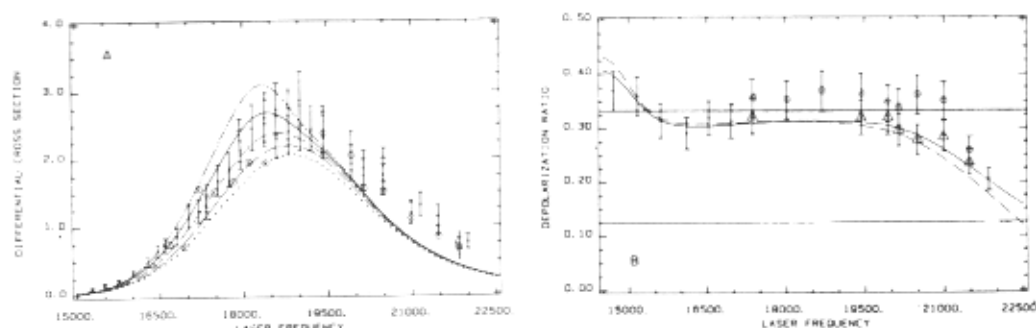


FIG. 7. (A) Calculated and experimental REPs for the I_2 fundamental in hexane plotted on an absolute scale, as in fig. 5 but with more data points and 15% error bars. These points were rescaled to our value of the absolute cross section at 5145 Å. The homogeneous linewidths, or damping factors, are as follows: ——— 12 cm^{-1} , — 15 cm^{-1} , --- 20 cm^{-1} , —·—·— 30 cm^{-1} , and + + + 50 cm^{-1} . The inhomogeneous linewidth and the solvent effect on the transition strength are both determined by the absorption spectrum. The D state is included in the calculation. (B) The calculated and experimental depolarization dispersion curves of the I_2 fundamental in hexane. The circled data points between 17,000 and 21,500 cm^{-1} represent the raw data at these frequencies. The triangles represent normalized data. Below 17,000 cm^{-1} and above 21,500 cm^{-1} there was no need to normalize the data. The error bars are drawn to $\pm 10\%$. The calculation parameters are as in (A) with $\Gamma = 15 cm^{-1}$. The solid line includes the D state contribution, while the dashed line neglects this contribution. The horizontal lines at 1/3 and 1/8 represent the depolarization ratios if only nondegenerate or doubly degenerate states, respectively, contribute to the Raman cross-sections.

the benzene 992 band. The calculated DDPs are in better agreement for the fundamental than for the first overtone (fig. 8) or the second overtone (not shown).

Various possibilities were tried to resolve the discrepancies between theory and calculation. Perhaps the most interesting of these considers the addition of an iodine-solvent charge-transfer state to the set of Raman-active states in order to raise the REP in the high-frequency wing. This possibility is subject to experimental test. We repeated our REP measurements in perfluorohexane and in chloroform¹⁵. Hexane is thought to have a contact charge-transfer state with I_2 in contrast to perfluorohexane, which is not

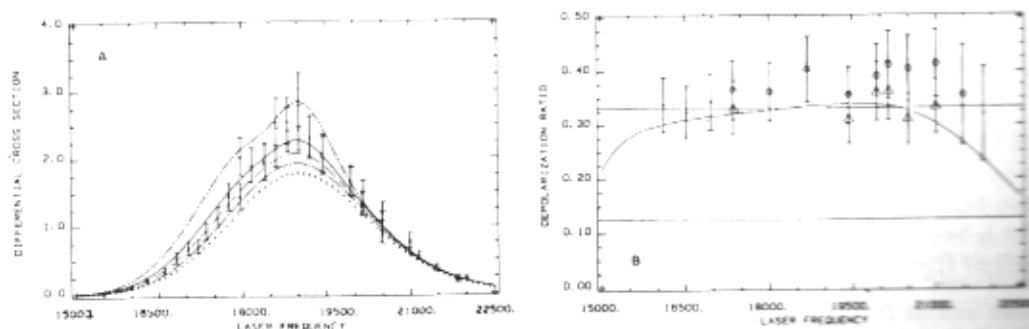


FIG. 8. The calculated and experimental REPs for the first overtone of I_2 in hexane. The error bars are drawn to $\pm 15\%$. The parameters are the same as in fig. 7 except that the ——— curve was calculated with $\Gamma = 10 cm^{-1}$.

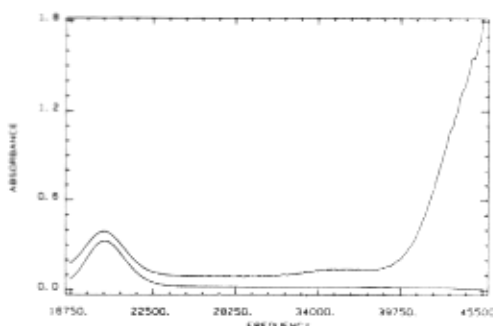


FIG. 9. The UV-visible absorption spectrum of I_2 in *n*-hexane and in perfluorohexane. The top spectrum is I_2 in *n*-hexane which has been offset by 0.08 absorbance units to distinguish the two spectra. Note the strong absorption band appearing in the UV spectrum of I_2 in hexane but not in the spectrum of I_2 in perfluorohexane.

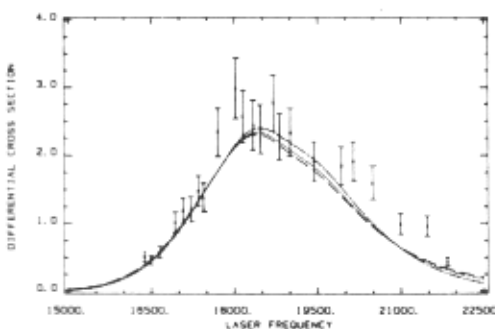


FIG. 10. The calculated and experimental REPs of the I_2 fundamental in perfluorohexane. The error bars are drawn to $\pm 10\%$. The curves were all calculated with $\Gamma = 15 \text{ cm}^{-1}$. The dashed line was calculated with the D state contribution with $|\mu_{XD}|^2 = 40 \text{ D}^2$, the solid line was calculated with $|\mu_{XD}|^2 = 25 \text{ D}^2$, and the dot-dashed line was calculated with no D state contribution.

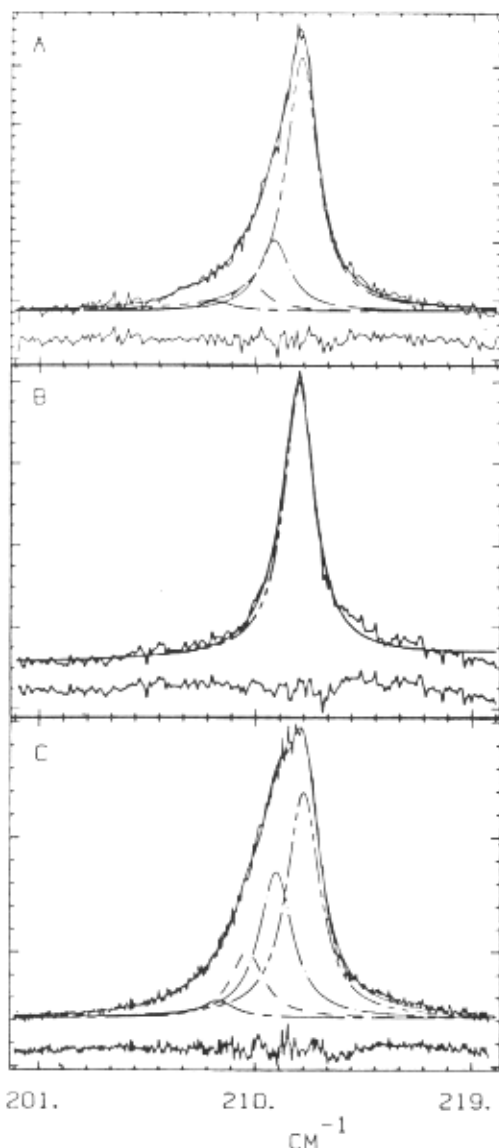


FIG. 11. Raman spectra of the I_2 fundamental fit with Lorentzian lines spaced according to the known anharmonicity of I_2 in hexane. The difference between the experimental spectrum and the total fit is plotted to scale beneath each spectrum. The contributions from the various initial states are as follows: $i = 0$ (-----), $i = 1$ (— · — · —), $i = 3$ (----) and $i = 4$ (— — — —). The excitation frequencies are (A) 4579 Å ($21,840 \text{ cm}^{-1}$), (B) 5145 Å ($19,435 \text{ cm}^{-1}$), and (C) 5945 Å ($16,810 \text{ cm}^{-1}$).

thought to have one²⁰. Chloroform should, of course, have a stronger charge-transfer complex than hexane. Figure 9 shows the UV-visible absorption spectrum of I_2 in both *n*-hexane and in perfluorohexane. It shows the absorption from the charge-transfer complex in hexane and the lack of such an absorption in perfluorohexane.

Figure 10 shows the REP of I_2 in perfluorohexane together with the results of the appropriate calculations. Calculations were again tried both with and without including the possible contribution of the D state. As the figure shows, the experimental points are higher than the theoretical ones, just as for the data in hexane. The results for chloroform are very similar.

It is remarkable that the fit of theory and experiment are so similar for the REPs of I_2 in *n*-hexane, *n*-perfluorohexane and chloroform. All of these give a width of about 15 cm^{-1} for the levels of the upper electronic states. This suggests that the width is due to simple thermal fluctuations of the solvents since the three solvents do not differ much in the magnitude of these fluctuations.

Let us go back and consider the curious phenomenon we mentioned at the beginning: the I_2 Raman bands shift with a change in exciting frequency. In all the work mentioned so far, we took spectra at relatively low resolution and ignored any small shifts. Now we consider spectra taken at higher resolution (fig. 1). Each Raman band is made up of both a transition to the ground vibrational state (for example, $1 \leftarrow 0$) but also hot bands ($2 \leftarrow 1$, $3 \leftarrow 2$, $2 \rightarrow 3$, etc.). Figure 11 shows a fit of such a hot band sequence to the observed bands taken with different exciting frequencies. It shows that the components that make up an individual vibration shift drastically with excitation and so appear to shift the vibrational band.

The observed bands can be resolved into components at each exciting frequency and so we can derive REPs for each component. Again we can compare with the results of calculations; such a comparison for the fundamental over a part of the frequency range is shown in fig. 12. Discrepancies between experiment and calculation are obvious at the low-frequency side of the data. Agreement is good in the middle and high-frequency side (not shown) and for the first overtone (not shown).

It is difficult to appreciate the details of the small shifts in the calculated REPs and DDPs due to a variety of causes and to compare all of these to the experimental results. Much more detail is available in the original papers¹³⁻¹⁶. Here, we summarize the highlights of our studies.

We have measured the REPs of the fundamental and first two overtones of I_2 in *n*-hexane and placed these profiles on an absolute intensity scale. We have also measured the absolute REP of the I_2 fundamental in perfluorohexane and placed the previously reported REPs of chloroform on an absolute intensity scale. We have measured both the depolarization dispersion profiles and relative intensities of the hot bands in the I_2 bands in hexane. We have compared all of these to calculations, based on gas phase values of the excited state parameters.

In all three solvents, the REPs fit best with an excited state homogeneous width of about 15 cm^{-1} , which translates into 0.3 ps. For each fundamental REP, the major

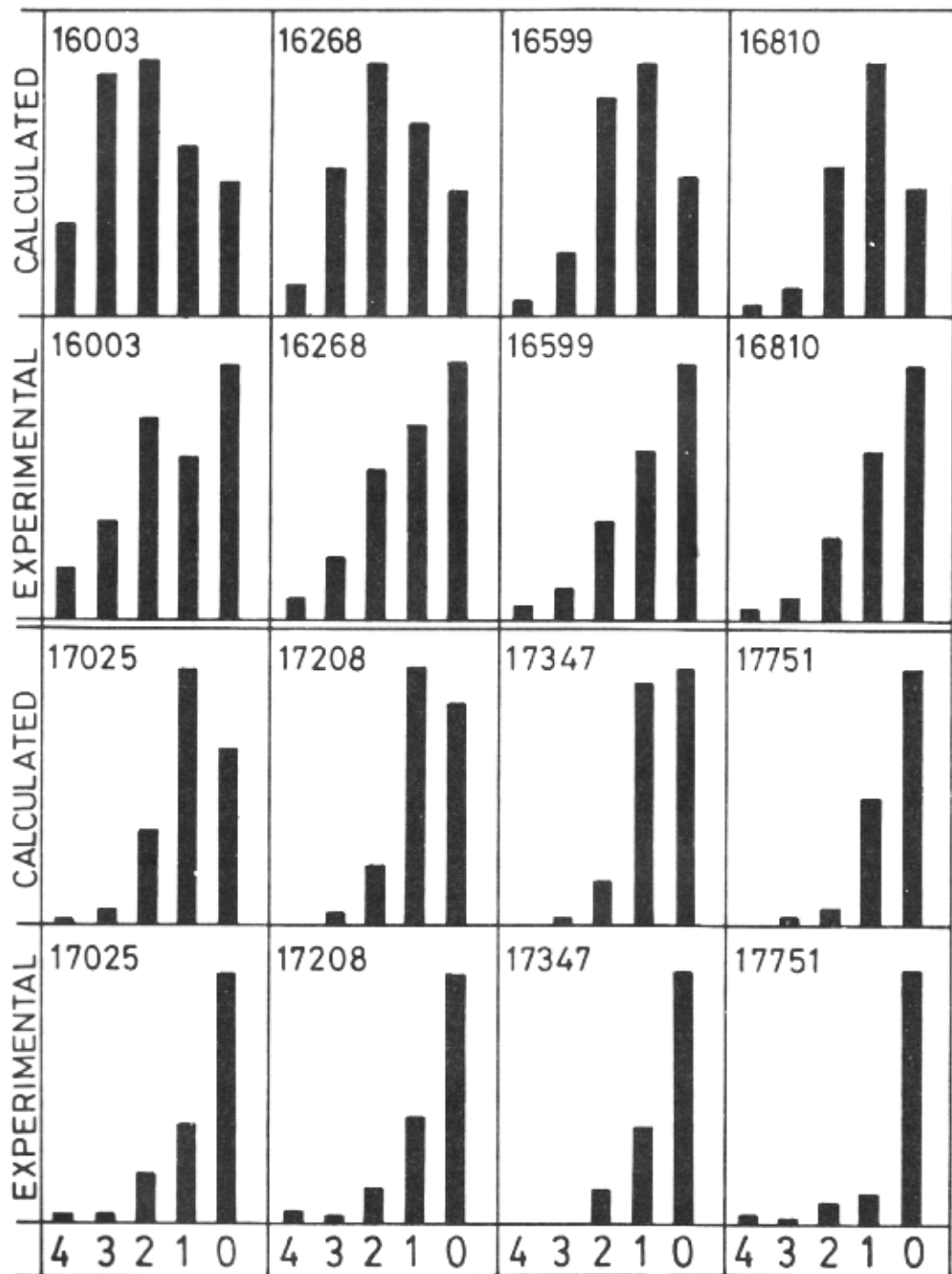


FIG. 12. The calculated and experimental bandshapes for the isotropic part of the I_2 fundamental. The intensity of the strongest transition at each listed excitation frequency is assigned a value of one, and the other transitions are drawn to this scale. The transitions are numbered by indicating the lower vibrational state, $\bar{\nu} = 15\text{ cm}^{-1}$ and the D state is included in the calculation.

discrepancy between calculation and experiment is in the high-frequency wing of the I₂ visible absorption band.

The calculated and experimental depolarization dispersion profiles are in good agreement, if it is assumed that the B" state is blue shifted about 100 cm⁻¹ relative to the B state. We note that this small 'shift' may well be due to inaccuracies in the gas phase values or to a solution shift. The consistently high experimental depolarization ratios are also explained, in part, by rotation of the I₂ molecule in the excited electronic state. The intensity distributions of the ground and hot band transitions show good agreement for the first overtone, but again there is disagreement for the fundamental.

It appears that there is a contribution missing from the calculation for the fundamental. Although the addition of another state to the calculation would tend to increase the intensity in the wings as needed to approve agreement, it would all decrease the peak of the REP. This would result from the effect of the cross term between the new state and the B state. Such a decrease is not observed. However, the addition of contributions from a number of further states plus small shifts in the I₂ potentials from those that occur for the isolated molecule will undoubtedly fit our data. More data are needed. The most useful would be in the UV region where the additional states are expected to lie. Another interesting direction is to consider the REPs and DDPs of much stronger I₂-benzene complexes, a direction we are now pursuing.

Acknowledgments

Dr. Roseanne J. Sension and Mr. Takamichi Kobayashi did the many painstaking experiments presented here. Dr. Sension developed and carried out the extensive calculations and put theory and experiment together. The National Science Foundation supported this work.

References

1. SENSION, R. J., SNYDER, R. G. AND STRAUSS, H. L. *Proc. Ninth Int. Conf. Raman Spectroscopy*, Tokyo, Japan, 1984, pp. 646-647.
2. TELLINGHUISEN, J. *J. Chem. Phys.*, 1982, **76**, 4736-4744; 1973, **58**, 2821.
3. MULLIKEN, R. S. *J. Chem. Phys.*, 1971, **55**, 288-309.
4. COXON, J. A. *Mol. Spectrosc.*, 1973, **1**, 177.
5. LUC, P. *J. Mol. Spectrosc.*, 1980, **80**, 41-55.
6. BERGSMA, J. P., BERENS, P. H., WILSON, K. R., FREDKIN, D. R. AND HELLER, E. J. *J. Phys. Chem.*, 1984, **88**, 612-619.

7. a. BECKMANN, E. *Z. Phys. Chem.*, 1890, **5**, 76-82.
b. HILDEBRAND, J. H. AND GLASCOCK, B. L. *J. Am. Chem. Soc.*, 1909, **31**, 26-31.
c. BENESI, H. A. AND HILDEBRAND, J. H. *ibid*, 1949, **71**, 2703-2707.
8. MULLIKEN, R. S. AND PERSON, W. B. *Molecular complexes*, Wiley, New York, 1969, especially pp. 156-161.
9. HYNES, J. T. *Ann. Rev. Phys. Chem.*, 1985, **36**, 573-597.
10. a. BERG, M., HARRIS, A. L. AND HARRIS, C. B. *Phys. Rev. Lett.*, 1985, **54**, 951-954.
b. HARRIS, A. L., BROWN, J. K. AND HARRIS, C. B. *Ann. Rev. Phys. Chem.*, 1988, **39**, 341.
11. SAKURAI, J. J. *Advanced quantum mechanics*, Addison-Wesley, Reading, Mass, 1967, Ch. 2.
12. YARIV, A. *Quantum electronics*, Wiley, New York, 1975, Ch. 8.
13. SENSION, R. J. AND STRAUSS, H. L. *J. Chem. Phys.*, 1986, **85**, 3791-3806.
14. SENSION, R. J., KOBAYASHI, T. AND STRAUSS, H. L. *J. Chem. Phys.*, 1987, **87**, 6221-6232.
15. SENSION, R. J., KOBAYASHI, T. AND STRAUSS, H. L. *J. Chem. Phys.*, 1987, **87**, 6233-6239.
16. SENSION, R. J. AND STRAUSS, H. L. *J. Chem. Phys.*, 1988, **88**, 2289.
17. MUKAMEL, S. *J. Chem. Phys.*, 1985, **82**, 5398-5408.
18. KIEFER, W. AND BERNSTEIN, H. J. *J. Raman Spectrosc.*, 1973, **1**, 417.
19. ROUSSEAU, D. L., FRIEDMAN, J. M. AND WILLIAMS, P. F. *Topics in current physics*, Springer, Berlin, 1979, Vol. 11, Ch. 6.
20. EVANS, D. F. *J. Chem. Phys.*, 1955, **23**, 1424-1428.

Inelastic light scattering in crystals

A. K. RAMDAS

Department of Physics, Purdue University, West Lafayette, IN 47907 USA.

Received on September 26, 1988.

(Extended Abstract of the talk given at the Raman Centenary Celebrations at the Indian Institute of Science, Bangalore on November 10, 1988)

In 1988, the year of the Raman birth centenary and the diamond jubilee of the discovery of the Raman Effect¹, it seems appropriate to recall Lord Rutherford's statement in his presidential address to the Royal Society²: "The Raman Effect must rank among the best three or four discoveries in experimental physics of the last decade. It has proved, and will prove an instrument of great power in the study of the theory of solids."

The nature of the one-phonon and multiphonon-Raman spectra (Rasetti & Fermi³; R. S. Krishnan⁴; Raman-Born controversy⁵); the LO-TO splitting of polar modes (Mathieu & Couture⁶); Brillouin scattering and elastic/elasto-optic constants (Krishnan⁷; Krishnan & Chandrasekharan⁸; Chandrasekharan⁹); symmetry (Bhagavantam & Venkatarayudu¹⁰); and soft modes and phase transitions (Raman & Nedungadi¹¹) represent some of the major contributions to inelastic light scattering in crystals during the pre-laser period.

The invention of the laser in 1960 and its application to Raman spectroscopy in 1962 have made inelastic light scattering a powerful tool in condensed-matter physics. With major innovations in techniques (photoelectric detection; optical multi-channel detector systems; holographic gratings; piezo-electrically scanned Fabry-Perot interferometers; tunable dye lasers, etc.), the scope of the field is now vastly extended. Collective and localized excitations of vibrational, electronic or magnetic nature have become accessible with Raman and Brillouin spectroscopy. Extreme physical conditions—high-magnetic fields, ultrahigh pressures—are experimentally tractable. Time-resolved Raman spectroscopy has profound applications for systems evolving with time scales as small as a Femto-second.

Personally I have thoroughly enjoyed the applications of Raman and Brillouin spectroscopy in semiconductor physics. Since the first report on the 'Raman scattering in silicon' by Russell¹², Raman scattering by polar phonons in compound semiconductors as well as their coupling with plasmons have been observed. Raman scattering from local modes; polaritons; donors and acceptors; free carriers in a magnetic field—all of these have extended and deepened our knowledge of semiconductor physics. Raman spectra of novel semiconductors like 'diluted magnetic semiconductors' and novel hetero-

structures (superlattices and multiple quantum wells) provide some of the most spectacular and delicate illustrations of the power of Raman spectroscopy.

In my talk I will focus on:

(1) **First and second-order Raman spectrum of diamond as well as the Brillouin components**^{13,14}: Interpretation in terms of the dispersion curves for the lattice vibrations determined by Warren *et al*¹⁵ using inelastic neutron scattering; absolute cross section of the Raman scattering; elastic and elasto-optic constants—these are the significant aspects of the phonon spectrum of diamond, a crystal of fundamental importance in condensed-matter physics.

(2) **Piezo-spectroscopy**¹⁶ **and the unusual aspects**¹⁷ **of the zone center optical phonons in α -quartz**: α -quartz has a rich Raman spectrum exhibiting one of the sharpest lines in Raman spectroscopy along with linear-q effects characteristic of polar phonons in crystals free of improper symmetry. Uniaxial stress effects—piezospectroscopy—is a powerful tool in the study of Raman spectra of crystals; this is illustrated with examples from the Raman spectrum of α -quartz.

(3) **Phase transition, mode softening, and zone-folding in crystalline benzil**¹⁸: Crystalline benzil ($C_6H_5COCOC_6H_5$) is an isomorph of α -quartz at room temperature. It undergoes a phase transition to a monoclinic (C_2^3) symmetry below $T_c = 84$ K. Associated with this phase transition the unit cell enlarges. The external modes of benzil show striking effects in the Raman spectrum.

(4) **Magnetic excitations in diluted magnetic semiconductors**¹⁹: Raman: electronic paramagnetic resonance and Raman: anti-ferromagnetic resonance are exhibited by the novel, tetrahedrally co-ordinated diluted magnetic semiconductors (e.g. $Cd_{1-x}Mn_xTe$). Mutual exclusion of Stokes and anti-Stokes spectrum; magnetically—and temperature-tuned resonance Raman Effect—such unusual, striking phenomena are displayed by these semiconductors.

References

1. RAMAN, C. V. *Indian J. Phys.*, **2**, 1928, 387.
2. RUTHERFORD, E. *Proc. R. Soc.*, 1931, **130A**, 239. The quotation appears on p. 259.
3. FERMI, E. AND RASETTI, F. *Z. Phys.*, 1931, **71**, 689.
4. KRISHNAN, R. S. *Proc. Indian Acad. Sci.*, 1947, **A26**, 399.
5. For Raman-Born controversy see R. Loudon, *Adv. Phys.*, 1964, **13**, 423.
6. COUTURE MATHIEU, L. AND MATHIEU, J. P. *Comptes Rendus*, 1953, **236**, 371.
7. KRISHNAN, R. S. *Proc. Indian Acad. Sci.*, 1955, **A41**, 91.
8. KRISHNAN, R. S. AND CHANDRASEKHARAN, V. *Proc. Indian Acad. Sci.*, 1950, **A31**, 427.

9. CHANDRASEKHARAN, V. *Proc. Indian Acad. Sci.*, 1950, **A32**, 379.
10. BHAGAVANTAM, S. AND VENKATARAYUDU, T. *Proc. Indian Acad. Sci.*, 1939, **A9**, 224.
11. RAMAN, C. V. AND NEDUNGADI, T. M. K. *Nature*, 1940, **145**, 147.
12. RUSSELL, J. P. *Appl. Phys. Lett.*, 1965, **6**, 223.
13. SOLIN, S. A. AND RAMDAS, A. K. *Phys. Rev.*, 1970, **B1**, 1687.
14. GRIMSDITCH, M. H. AND RAMDAS, A. K. *Phys. Rev.*, 1975, **B11**, 3139.
15. WARREN, J. L., YARNELL, J. L., DOLLING, G. AND COWLEY, R. A. *Phys. Rev.*, 1966, **158**, 805.
- 16a. TEKIPPE, V. J., RAMDAS, A. K. AND RODRIGUEZ, S. *Phys. Rev.*, 1973, **B8**, 706.
- b. BRIGGS, R. J. AND RAMDAS, A. K. *Phys. Rev.*, 1977, **B16**, 3815.
17. GRIMSDITCH, M. H., RAMDAS, A. K., RODRIGUEZ, S. AND TEKIPPE, V. J. *Phys. Rev.*, 1977, **B15**, 5869.
18. MOORE, D. R., TEKIPPE, V. J., RAMDAS, A. K. AND TOLEDANO, J. C. *Phys. Rev.*, 1983, **B27**, 7676.
19. RAMDAS, A. K. AND RODRIGUEZ, S. in *Diluted magnetic semiconductors*, Vol. 25 of Semiconductors and semimetals, ed. J. K. Furdyna and J. Kossut, Academic Press, 1988, pp. 345-411.

Selected papers of Raman: An introduction

T. V. RAMAKRISHNAN

Department of Physics, Indian Institute of Science, Bangalore 560 012.

A small selection of papers by Professor C. V. Raman follows this introduction. Some have been selected for their immediate as well as lasting impact, others for their prescience. They illustrate his characteristically direct and incisive approach, his interest in natural phenomena, his concern for basic questions and implications, and his eye (and ear) for beauty.

Raman's writing style is direct, clear and has a characteristic literary flavour. For these reasons annotating his papers is often an undesirable intrusion. However, many of them are very brief, and were written in a certain intellectual milieu for a particular audience. Several papers hint at areas of physics which have seen growth much later. In this introduction, I try therefore to expand on the matter condensed in a few lines, to set out the background, or to point out how the work foreshadows present concerns in physics.

The very first paper [P1] is an extremely brief and incomplete summary of one of Raman's two major contributions to musical acoustics, namely his work on the Mridangam (and the Tabla). These Indian drums are true musical instruments, the musical quality being due to the harmonic overtones and their relative intensities, as well as to the clarity, duration and volume of sound. Now in a simple circular drum, the overtones are not integral multiples of a fundamental or lowest frequency mode of vibration. It is therefore not musical. Raman guessed that the Indian drum is designed (with its nonuniform black centre and an auxiliary circular leather strip) to produce harmonic overtones, to damp out high-frequency harmonics and to produce clear long-lasting notes. He showed this by exciting various harmonics, and determined their vibration patterns by noting the places where sand, spread on the drum, collects. (It collects at places which do not vibrate, called nodes; their number and shape are diagnostic of the frequency and nature of the mode of vibration). This note does not detail or even describe these results. They were written up much later, in 1934 [The Indian musical drums, *Proc. Indian Acad. Sci.*, 1934, **1**, 179-188], though all the major results had been obtained before 1921. The reason for this delay was Raman's increasing preoccupation with light and its scattering, the beginnings of which can be seen in the next paper. Anyone interested in the area of musical acoustics should read his 1934 paper. It describes Raman's discoveries in detail, with pictures of the drum in various 'pure' modes of vibration.

The second paper, on 'The colour of the sea' [P2] is a Raman classic. A great scientist, Lord Rayleigh (whom Raman particularly admired) said, perhaps without thinking much about it, that the blue of the sea is just the reflected blue of the sky. Raman, on his first voyage abroad, disposed of this suggestion quickly with a few deckside observations using a Nicol prism analyzer. The idea is the following: the light reflected from water is partially polarized, the polarization being nearly complete for a certain angle of incidence. The Nicol prism, if oriented in a particular direction, will completely block out polarized light. By this simple arrangement, reflected light can be eliminated. Raman found, under these conditions, that the blue of the sky instead of disappearing was 'wonderfully improved'! His belief that the blue of the ocean had the same physical cause as the blue of the sky (explained by Lord Rayleigh!) was reinforced by two observations. The first is that when the reflected light is cut out, the colour of the sea depends on the angle between the incident sunlight and the sea-scattered light reaching the eye. Further, the track of sunlight in water could be seen under certain conditions out to considerable depth. Now, Lord Rayleigh had argued that the blue of the sky is due to scattering of sunlight in the following way. Purely statistically, at a given instant some regions of air are denser, some others rarer. Since the refractive index of air depends on density, these spontaneous density fluctuations mean that the refractive index fluctuates randomly. This scatters sunlight; the extent or intensity of scattering depends on angle as well as on light wavelength, increasing inversely as the fourth power of the latter. Thus the blue part of sunlight is scattered much more than the longer wavelength parts. There is every reason to expect that similar fluctuations in density should occur in water as well and so the same scattering process should be operative. Raman pursued this idea vigorously, and produced a fairly detailed analysis of the colour of the sea rather soon (*Proc. R. Soc.*, 1922, **A101**, 64–80, and a monograph entitled 'Molecular diffraction of light' published by the Calcutta University in 1922). The point is that this scattering is due not to extraneous causes such as dust or other substances, but is due to density fluctuations.

Raman's sustained efforts at observing this Rayleigh scattering in dust-free fluids in the laboratory originate with this experience. These bore fruit in several spectacular ways. Some of these are subjects of the next few reprints.

Raman was probably the first person to appreciate the implications of light scattering from glassy or amorphous solids, and viscous liquids. Glasses are generally made by rapidly cooling melts or liquids, the cooling rate being large enough to prevent crystallization or formation of the crystal. If the arrangement of atoms in the glass is just the same as in the melt, but is frozen-in, then light would be scattered from the frozen-in density fluctuations appropriate to that for the melt *i.e.* the liquid. Another possibility is that atoms in a glass are positionally well ordered, almost as in the corresponding crystal, but that the constituent anisotropic molecules are not orientationally ordered, *i.e.* there are considerable orientational fluctuations (frozen-in again). A third possibility is that especially in chemically complex glasses (*e.g.* optical or window glass) there are sizeable compositional fluctuations. In general, things tend to separate out at low temperatures (entropy is less at lower temperatures!) so that these compositional fluctuations tend to increase on cooling. In a particular glass, all these effects could be present to different degrees at different length (and time) scales.

In the very first brief paper on the subject [P3] Raman argued, from the rather large Rayleigh-like scattering of light in glasses, that there are sizeable frozen-in density fluctuations in them, comparable to those in liquids. Thus a quasicrystalline model for the glassy state, with sizeable crystallites, is ruled out. To confirm for himself the hypothesis that the scattering of light from glasses is due to intrinsic fluctuations and not accidental 'inclusions' and inhomogeneities, Raman took a dozen optical glasses with graded refractive indices and studied the intensity and the depolarization of light scattered from these [P11]. He found that the former increases and the latter decreases as the refractive index increases. This systematic dependence suggests that the scattering process at work is intrinsic, related to their 'optical density' and is not extrinsic. These contributions mark the beginning of a powerful way of probing a class of systems and phenomena not fully understood yet.

Glasses are strange systems which have fallen out of thermal equilibrium in regard to some degrees of freedom (or configurations) and are in equilibrium as far as other degrees of freedom (*e.g.* local atomic vibrations) are concerned. That is, the distribution of energy in some arrangements of atoms or molecules cannot be described by a temperature, while for some other arrangements it can be! The dynamics of this process, *i.e.* how it occurs, is an area of great current interest. Light-scattering techniques are much more sophisticated now and time-dependent processes are routinely studied. Fascinating very slow relaxation processes have been uncovered. However, one still does not have a deep understanding of these phenomena which are common to all glasses.

Another contribution in the same general area is light scattering from viscous liquids [P9]. Raman was fascinated by the following idea, due primarily to Brillouin. The thermal (temperature-induced) agitation of atoms in a liquid (more clearly in a solid) can be thought of a sum (or superposition) of sound waves of different wavelengths, amplitudes and directions of propagation. Scattering of light from one such wave will lead to a light wave with a slightly different (shifted) direction of propagation and nearly the same frequency just as happens when light is incident on a diffraction grating. This Brillouin line was looked for by Raman and coworkers. Now if the sound wave damps out quickly, such a distinct line won't be seen. The damping is due to viscous friction in a liquid, and will thus decrease as temperature increases (and fluid viscosity decreases). Thus on increasing the temperature of a liquid, the Brillouin line should appear; this was exactly what Raman and Raghavendra Rao found. This also is an active current area of research; one would like to probe and understand the way the Brillouin line disappears as one approaches the glass transition marked by a catastrophic viscosity increase.

The paper on optical behaviour of protein solutions [P5] is again well ahead of its time. Whereas large protein molecules in solution were thought of as particles of dust leading to haze or light scattering, Raman considered them to be a gas of particles with a temperature, compressibility, etc. It turns out that this gas or fluid changes its nature (*e.g.* from gas to liquid) as its density, or the medium in which the molecules are suspended, changes. At such a transition point, fluctuations in density are very prominent, and we expect the same excess scattering of light as occurs for example at the

liquefaction point of carbon dioxide. The study of phase changes in polymers, colloids and gels has emerged as a major field and light scattering is an important tool for monitoring molecular movements, arrangements and cooperative changes. This was probably the first paper in which one such object (protein solution) was thought of as a thermodynamic system.

Raman's interest in understanding the arrangement of molecules in dense systems such as liquids led to the pioneering use of X-ray scattering (diffraction) for probing their structure. Raman and Ramanathan had realized in 1923 that since X-rays have wavelengths of molecular dimensions, small-angle scattering is related to the statistical density fluctuations described earlier but large-angle scattering is a direct probe of local molecular arrangement. This large-angle scattering shows up as haloes [P4]. Raman and Sogani compared the haloes for two organic compounds, hexane and cyclohexane, and argued that the differences are due to specific differences in molecular shape. This is the first work on X-ray diffraction as a structural tool in liquids. The work would have been complete if the authors had realized that the Fourier transform $g(r)$ of the observed intensity $S(q)$ (as a function of wavevector change q) gives the two-particle correlation function or the probability of finding two molecules a distance r apart, a quantity of direct physical appeal. This was done by Zernicke and Prins in 1927.

The papers P6, P7 and P12 describe the most celebrated contribution of Raman to science, namely the Raman Effect. Raman, his students, and coworkers had been investigating the scattering of light from liquids since 1921 or so. Most observations, some of which have been described above, could be explained by assuming light to be a classical wave scattered by spontaneous fluctuations in the medium. However one persistent phenomenon did not fit into this pattern; it was dubbed 'weak fluorescence' to begin with. Clues about its nature and evidence for its general occurrence, were obtained over the years. One such is the following. By using a pair of complementary filters, *i.e.*, filters such that one filter blocks the colours that the other transmits, Raman and Krishnan found the following: When both the filters are placed in the path of the beam incident on the pure fluid no scattered light is seen. However, if one filter is placed in the path of the incident beam and the other in the path of the scattered beam, some weak fluorescence could be seen. This clearly means that the colour (or wavelength) of the light transmitted by the first filter changes on scattering by the fluid so that it is no longer exactly complementary to the other filter and is therefore not fully blocked by it. Raman was reinforced in this belief by the then recently discovered Compton Effect in which the wavelength of X-rays hitting a 'free' electron is changed. He reasoned that there could be an optical analogue of the Compton Effect, namely that a light wave changes its wavelength (or frequency or energy) on being scattered by an atom or molecule. To check this, a source emitting light of a single colour or wavelength is needed. An intense mercury vapour lamp with proper filters is such a monochromatic source. When the scattered light was viewed by a spectroscope (in which light of different wavelengths shows up as differently placed lines) Raman found, in addition to the line corresponding to the original wavelength, another line with a shifted (increased) wavelength. In some substances, more

than one line was seen; there were also lines with reduced wavelength. The spectra were recorded, and the papers reprinted here show some of them.

Why is this 'new radiation' important? With his uniquely well-prepared mind, Raman understood it all. Firstly, it is striking evidence for the quantum nature of light. A light quantum hits a molecule, and excites one of its internal modes. The remaining electromagnetic energy comes out as a light quantum or photon of reduced energy or increased wavelength. If the light quantum absorbs a quantum of internal molecular excitation, the outgoing photon has higher energy or shorter wavelength. Thus Einstein's ideas (put forward to explain the photoelectric effect) that light energy is carried in quanta, and that this energy is equal to (hc/λ) where h is a constant called Planck's constant, c the velocity of light and λ the wavelength, are strongly supported. At a more detailed level, Raman realized that the polarizability of the molecule was involved in the mechanism. (This is the same property which causes the refractive index of the liquid to differ from unity and to depend on light wavelength). Indeed, he realized that a detailed theory of molecular and atomic polarizability, due to Kramers and Heisenberg, suggested the possibility of such an effect.

The other major implication, clear to Raman, was that here was a tool of great convenience, precision and power for studying internal excitations of molecules, *e.g.* their vibrations, rotations, and electronic-excited states. Instead of studying the former by direct absorption in the infrared and far-infrared, one could conveniently investigate them in the optical region, as energy differences. Now molecular structure and binding are the backbone of chemistry, so he foresaw that this new branch of spectroscopy would be important for chemistry. With the advent of lasers (monochromatic light sources of great intensity and coherence) Raman spectroscopy became a standard physico-chemical technique.

The availability of lasers has brought about an explosive increase in the number of light-scattering experiments, as several articles in this volume describe. In his Nobel lecture, Raman said: "The universality of the phenomenon, the convenience of the experimental technique and the simplicity of the spectra obtained enable the effect to be used as an experimental aid to the solution of a wide range of problems in physics and chemistry. Indeed, it may be said that it is this fact which constitutes the principal significance of the effect. The frequency differences from the spectra, the width and character of the lines appearing in them, and the intensity and state of polarization of the scattered radiations enable us to obtain an insight into the ultimate structure of the scattering substance. As experimental research has shown, these features in the spectra are very definitely influenced by physical conditions, such as temperature and state of aggregation, by physico-chemical conditions, such as mixture, solution, molecular association and polymerization, and most essentially by chemical constitution. It follows that the new field of spectroscopy has practically unrestricted scope in the study of problems relating to the structure of matter. We may also hope that it will lead us to a fuller understanding of the nature of light, and of the interactions between matter and light". The prophecy has been fulfilled, I think even beyond the dreams of its visionary discoverer.

The paper in this collection on anomalous diamagnetism [P8] is an example of the quickness and richness of Raman's scientific imagination. Diamagnetism is due to electrons circulating in closed (atomic) orbits. Ehrenfest had suggested that the large diamagnetism of bismuth implied that in crystalline Bi electron orbits are specially large. Raman argues in this paper that many facts *e.g.* large change of electrical resistance in magnetic field, anomalous Hall Effect, large change of size in a magnetic field, change of these properties with temperature, are all connected with this. Now with hindsight (as well as the idea of holes and an extremely detailed knowledge of electronic states in Bi) it appears that many of the suggestions are not correct, but let us just look at the quick reach!

The paper with Nagendra Nath [P13] is one of a series of five, in which a phenomenon first observed by several others, was analyzed in a characteristically direct fashion. A high-frequency sound wave propagates in a liquid, and on being reflected by a plane boundary wall, forms stationary waves, or fixed sinusoidal patterns of lower and higher liquid density (and hence refractive index). Now suppose a plane light beam is incident on this. It will be diffracted. The pattern of intensity of diffracted light is observed to be very complex, with a large number of maxima and minima, and considerable wandering of their relative intensities as the angle of light incidence or sound wavelength are varied. Raman and Nath assumed to begin with that the periodic change in refractive index affects only the phase of the plane wavefront sinusoidally. Thus the outcoming wavefront is no longer planar, but corrugated. They calculated diffracted beam intensities, and showed that the complex observations are explained simply. In further work, the assumption that only the phase changes (valid if the light wavelength is much shorter than the sound wavelength) was given up, and amplitude modulation also considered. This whole work is remarkable for its perfection (a well-defined, interesting and rich phenomenon was completely explained theoretically), for its prototypical nature, and because it is a primarily theoretical contribution from a great experimenter. (Contrary to popular belief Raman not only had a sure and creative grasp of theoretical concepts and principles, he was also conversant with theoretical methods, and of course in detail with the great masters *e.g.* Rayleigh, Helmholtz, as well as with the theoretical papers of relevance to his interests).

The latest paper reprinted here [P10] reports a discovery: the soft mode. Many crystalline solids change their structure as a function of temperature, pressure, or both. If the change or transition is continuous, one can imagine a particular distortion or movement of atoms leading to the new structure. Now in a crystalline, harmonic solid, all arrangements of atoms can be described in terms of normal modes of atomic oscillations about a mean position. Thus as the point of transition is approached, that mode of oscillation which corresponds to the displacements leading to the new structure becomes soft, *i.e.* easily excited or of low frequency. This was exactly what Raman and Nedungadi observed in quartz. The particular lattice-vibration mode corresponding to the symmetry change ($\alpha \rightarrow \beta$ quartz) was seen to become softer and softer as the transition temperature T is approached. In the 1960s Cochran as well as Anderson showed that the square of the soft mode frequency is proportional to $(T - T_c)$. The subject of structural transitions and

soft modes saw considerable activity in the two decades 1960–1979; the pioneering work of Raman and Nedungadi was noted to be the beginning of it all.

I am thankful to Professors P. S. Narayanan, S. Ramaseshan, and C. N. R. Rao for help and advice about the selection of papers, and to Professor Ramaseshan for a conversation regarding Raman's contributions as well as style.

Selected papers of Raman

Contents

[P1]	Musical drums with harmonic overtones, <i>Nature</i> , 1920, 104 , 500 (with Sivakali Kumar)	519
[P2]	The colour of the sea, <i>Nature</i> , 1921, 108 , 367.	519
[P3]	Molecular structure of amorphous solids, <i>Nature</i> , 1922, 109 , 138-139.	520
[P4]	X-ray diffraction in liquids, <i>Nature</i> , 1927, 119 , 601 (with C. M. Sogani).	521
[P5]	Optical behaviour of protein solutions, <i>Nature</i> , 1927, 120 , 158.	521
[P6]	A change of wave-length in light scattering, <i>Nature</i> , 1928, 121 , 619.	522
[P7]	The optical analogue of the Compton Effect, <i>Nature</i> , 1928, 121 , 711 (with K. S. Krishnan).	522
[P8]	Anomalous diamagnetism, <i>Nature</i> , 1929, 124 , 412.	523
[P9]	Light scattering and fluid viscosity, <i>Nature</i> , 1938, 141 , 242-243 (with B. V. Raghavendra Rao).	523
[P10]	The $\alpha - \beta$ transformation of quartz, <i>Nature</i> , 1940, 145 , 147 (with T. M. K. Nedungadi).	525
[P11]	The scattering of light in amorphous solids, <i>J. Opt. Soc. Am.</i> , 1927, 15 , 185-189.	526
[P12]	A new radiation, <i>Indian J. Phys.</i> , 1928, 2 , 387-398.	531
[P13]	The diffraction of light by high frequency sound waves: Parts I & II, <i>Proc. Indian Acad. Sci.</i> , 1935, A2 , 406-420 (with N. S. Nagendra Nath).	544

The *Journal of the Indian Institute of Science* is grateful to *Nature*, the *Journal of the Optical Society of America*, the *Indian Journal of Physics*, the *Proceedings of the Indian Academy of Sciences* for granting permission to reproduce the above papers.

[P1]

[JANUARY 15, 1920

NO. 2620, VOL. 104] 500

Musical Drums with Harmonic Overtones.

It is well known that percussion instruments as a class give inharmonic overtones, and are thus musically defective. We find on investigation that a special type of musical drum which has long been known and used in India forms a very remarkable exception to the foregoing rule, as it gives harmonic overtones having the same relation of pitch to the fundamental tone as in stringed instruments. Five such harmonics (inclusive of the fundamental tone) can be elicited from the drumhead in this type of instrument, the first, second, and third harmonics being specially well sustained in intensity and giving a fine musical effect. The special method of construction of the drumhead which secures this result will be understood from the accompanying illustration (Fig. 1). It will

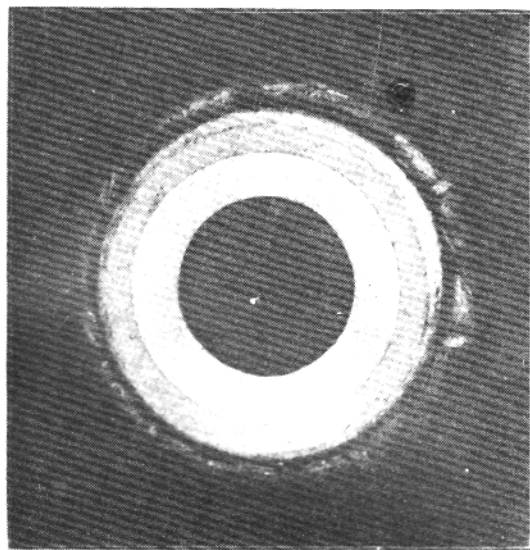


FIG. 1.—Drumhead giving harmonic overtones.

be noticed (1) that the drumhead carries a symmetrical distributed load, decreasing in superficial density from the centre outwards (this appears as a dark circle in the middle of the membrane, the load consisting of a firmly adherent but flexible composition, in which the principal constituent is finely divided metallic iron); and (2) that a second membrane in the form of a ring is superimposed on the circular membrane round its margin.

The character of the vibrations of this heterogeneous membrane which give rise to its remarkable acoustic

properties have been investigated by us. It is found, as might have been expected, that the fundamental pitch and the octave are derived respectively from the modes of vibration of the membrane without any nodal lines and with one nodal diameter. The third harmonic, we find, owes its origin to the fact that the next two higher modes of vibration of the drumhead (those with two nodal diameters and with one nodal circle respectively) have identical pitch, this being a twelfth above the fundamental. There is reason to believe that the fourth and fifth harmonics similarly arise from some of the numerous more complex modes of vibration of the drumhead becoming unified in pitch in consequence of the distributed load at the centre and round the periphery of the membrane. The central load also improves the musical effect by increasing the energy of vibration, and thus prolonging the duration of the tones.

C. V. RAMAN.

SIVAKALI KUMAR.

210 Bowbazaar Street, Calcutta, India,
December 10.

[P2]

NOVEMBER 17, 1921]

NO. 2716, VOL. 108] 367

The Colour of the Sea.

THE view has been expressed that "the much-admired dark blue of the deep sea has nothing to do with the colour of water, but is simply the blue of the sky seen by reflection" (Rayleigh's *Scientific Papers*, vol. 5, p. 540, and *NATURE*, vol. 83, p. 48, 1910). Whether this is really true is shown to be questionable by a simple mode of observation used by the present writer, in which surface-reflection is eliminated, and the other factors remain the same. The method is to view the surface of the water through a Nicol's prism, which may for convenience be mounted at one end of a tube so that it can be turned about its axis and pointed in any direction. Observing a tolerably smooth patch of water with this held in front of the eye at approximately the polarising angle with the surface of the sea, the reflection of the sky may be quenched by a suitable orientation of the Nicol. Then again, the sky-light on a clear day in certain directions is itself strongly polarised, and an observer standing with his back to the sun when it is fairly high up and viewing the sea will find the light reflected at all incidences sufficiently well polarised to enable it to be weakened or nearly suppressed by the aid of a Nicol.

Observations made in this way in the deeper waters of the Mediterranean and Red Seas showed that the colour, so far from being impoverished by suppression of sky-reflection, was wonderfully improved thereby. A similar effect was noticed, though somewhat less conspicuously, in the Arabian Sea. It was abundantly clear from the observations that the blue

colour of the deep sea is a distinct phenomenon in itself, and not merely an effect due to reflected sky-light. When the surface-reflections are suppressed the hue of the water is of such fullness and saturation that the bluest sky in comparison with it seems a dull grey.

By putting a slit at one end of the tube and a grating over the Nicol in front of the eye, the spectrum of the light from the water can be examined. It was found to exhibit a concentration of energy in the region of shorter wave-lengths far more marked than with the bluest sky-light.

Even when the sky was completely overcast the blue of the water could be observed with the aid of a Nicol. It was then a deeper and fuller blue than ever, but of greatly enfeebled intensity. The altered appearance of the sea under a leaden sky must thus be attributed to the fact that the clouds screen the water from the sun's rays rather than to the incidental circumstance that they obscure the blue light of the sky.

Perhaps the most interesting effect observed was that the colour of the water (as seen with the Nicol held at the polarising angle to the surface of the water and quenching the surface-reflection) varied with the *azimuth* of observation relatively to the plane of incidence of the sun's rays on the water. When the plane of observation and the plane of incidence were the same, and the observer had his back to the sun and looked down into the water, the colour was a brilliant, but comparatively lighter, blue. As the plane of observation is swung round the colour becomes a deeper and darker blue, and at the same time decreases in intensity, until finally when the plane of observation has swung through nearly 180° the water appears very dark and of a colour approaching indigo. Both the colour and the intensity also varied with the altitude of the sun.

The dependence of the colour on the azimuth of observation cannot be explained on a simple absorption theory, and must evidently be regarded as a *diffraction* effect arising from the passage of the light through the water. Looking down into the water with a Nicol in front of the eye to cut off the surface-reflections, the track of the sun's rays could be seen entering the water and appearing by virtue of perspective to converge to a point at a considerable depth inside it. The question is: What is it that diffracts the light and makes its passage visible? An interesting possibility that should be considered in this connection is that the diffracting particles may, at least in part, be the *molecules* of the water themselves. As a rough estimate, it was thought that the tracks could be seen to a depth of 100 metres, and that the intensity of the light was about one-sixth of that of the light of the sky from the zenith. If we assume that clear water, owing to its molecular structure, is capable of scattering light eight times as strongly as dust-free air at atmospheric pressure, it is clear that the major part of the observed effect may arise in this way.

It is useful to remember that the reflecting power of water at normal incidence is quite small (only 2 per cent.), and becomes large only for very oblique reflection. It is only when the water is quite smooth and is viewed in a direction nearly parallel to the surface that the reflected sky-light overpowers the light emerging from within the water. In other cases the latter has a chance of asserting itself.

C. V. RAMAN.

S.S. Narkunda, Bombay Harbour,
September 26.

[P3]

[FEBRUARY 2, 1922

NO. 2727, VOL. 109] 138, 139

Molecular Structure of Amorphous Solids.

A QUESTION of fundamental importance in the theory of the solid state is the nature of the arrangement of the ultimate particles in amorphous or vitreous bodies, of which glass is the most familiar example. Is it to be supposed that the molecules are packed together at more or less uniform distances apart, as in crystals, the orientation of individual molecules or of groups of molecules being, however, arbitrary? Or, on the other hand, is the spacing of the molecules itself irregular, the solid exhibiting in a more or less permanent form local fluctuations of density similar to those that arise *transitorily* in liquids owing to the movement of the molecules? The physical properties of amorphous solids, notably their softening and viscous flow below the temperature of complete fusion, would tend to support the latter view, but the possibility of a closer approximation to the crystalline state should not entirely be ruled out, especially in view of the very interesting recent work of Lord Rayleigh on the feeble double refraction exhibited by fused silica (Proc. Roy. Soc., 1920, p. 284). A good deal might be expected to depend on the nature of the material, its mode of preparation, and heat treatment. A material formed by simple fusion and re-solidification of comparatively simple molecules, such as silicon dioxide, might stand on a different footing from a material such as ordinary glass built up by chemical action and formation of complex silicates.

If the arrangement of molecules in a vitreous body were irregular, the local fluctuations of optical density would result in a strong scattering of a beam of light passing through it, the intensity of such scattering being comparable with that occurring in the liquid state at the temperature of fusion of the material (see note by the present writer in NATURE of November 24 last, p. 402). On the other hand, if the arrangement of the molecules approximated to the crystalline state the scattering of light would be merely that due to the thermal movements of the molecules and would be much smaller. As a matter of fact, glasses exhibit

a very strong scattering of light, some 300 to 500 times as strong as in dust-free air, the Tyndall cone being of a beautiful sky-blue colour and nearly, but not quite, completely polarised when viewed in a transverse direction. (Some glasses exhibit a green, yellow, or pink fluorescence when a beam of sunlight is focussed within them, and cannot be used for the present purpose; the fluorescence, even when very feeble, can be detected by the difference in colour of the two images of the Tyndall cone seen through a double-image prism.) Rayleigh, who observed the light-scattering in glass, attributed it to inclusions, some of which he assumed must be comparable in size with the wave-length (*Proc. Roy. Soc.*, 1919, p. 476). The closest scrutiny through the microscope under powerful dark-ground illumination fails, however, to indicate the presence of any such inclusions, and it seems more reasonable to assume, in view of the foregoing remarks, that the scattering is really molecular. Its magnitude is of the order that might be expected on the basis of a non-uniform distribution of the molecules.

Further observations with specially prepared glasses and with fused silica would be of great interest to investigate the influence of the chemical constitution and heat treatment on the molecular texture of the solid.

C. V. RAMAN.

210 Bowbazaar Street, Calcutta, December 29.

[P4]

APRIL 23, 1927]

No. 2999, VOL. 119] 601

X-ray Diffraction in Liquids.

In order to find experimental support for the theory of X-ray diffraction in liquids put forward some three years ago by C. V. Raman and K. R. Ramanathan (*Proc. Indian Association for the Cultivation of Science*, vol. 8, p. 127, 1923), extensive studies have been undertaken in the authors' laboratory of the phenomena observed when a pencil of monochromatic X-rays passes through a layer of fluid, particularly with the view of determining how the effects are influenced by the physical condition and the chemical nature of the substance under investigation. The photographs here reproduced (Fig. 1, *a* and *b*) were obtained in the course of work on this line by one of us (C. M. Sogani) and represent the X-ray liquid-haloes of hexane and cyclo-hexane respectively. The fluids were contained in cells with very thin walls of mica, and the K-radiation of copper from a Shearer X-ray tube was used.

The differences between the two patterns are sufficiently striking; cyclo-hexane shows a bright and sharply defined halo with a very clear dark space within, while hexane, on the other hand, shows a less intense and relatively diffuse halo, the inner margin

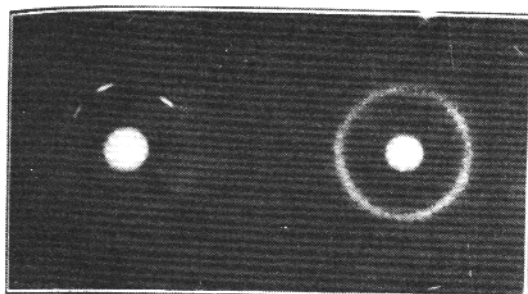


FIG. 1.—X-ray diffraction haloes of liquids.
a, Hexane; *b*, cyclo-hexane.

of which is not sharply terminated but extends almost up to the direction of the incident rays. These differences indicate very clearly the effect of the geometrical form of the molecules on the X-ray scattering by a liquid. From an X-ray point of view, cyclo-hexane consisting of ring-formed—though arbitrarily orientated—molecules has a nearly homogeneous structure, while on the other hand the elongated shape and varying orientations of the molecules in hexane cause it to be much less homogeneous in X-ray scattering. This explanation is supported by the observation that the diffraction halo of benzene resembles very closely that of cyclo-hexane.

It is very interesting to contrast these facts with the optical behaviour of the three liquids with regard to the scattering of ordinary light. Optically, hexane and cyclo-hexane are far more nearly similar to each other, and differ strikingly from benzene, the depolarisation of the scattered light being small for hexane and cyclo-hexane and relatively large for benzene. Here, evidently, the geometrical form of the molecule is of much less importance than its chemical character.

Further studies of the liquid-haloes for various organic substances of the aromatic and aliphatic series, and specially with the long-chain compounds, are in progress.

C. V. RAMAN.

C. M. SOGANI.

210 Bowbazaar Street,
Calcutta, India, Feb. 10.

[P5]

[JULY 30, 1927]

No. 3013, VOL. 120] 158

Optical Behaviour of Protein Solutions.

A VERY remarkable increase in light-scattering power is exhibited by gelatine solutions when the hydrogen-ion concentration approaches the value (about pH = 5) corresponding to the iso-electric point. This effect, which appears to have been known for

some time, has been recently studied in detail by Kraemer and his co-workers, who give interesting curves showing the manner in which the Tyndall effect varies with pH and temperature ("Colloid Symposium Monograph," vol. 4, and *Journal of Physical Chemistry*, May 1927).

The phenomena are scarcely intelligible on the view commonly adopted that the Tyndall effect in a colloidal solution is simply proportional to the number of scattering particles of the same kind present in it. Their explanation becomes clearer if we apply to colloidal solutions the general thermodynamic theory of light scattering, in which the Tyndall effect is regarded as due to local fluctuations of optical density in the medium. According to the latter theory, the scattering power of a colloidal solution would be connected with the osmotic pressure P of the particles, by the relation

$$\frac{\pi^2 RT}{2N\lambda^4} \frac{k(\partial\epsilon/\partial k)^2 p/m}{\partial P/\partial k}, \quad \dots \quad (1)$$

where k is the concentration of the dispersed material, ϵ is the optical dielectric constant of the solution and p/m is practically unity for a dilute solution. It is well known from the work of Jacques Loeb that the osmotic pressure of a gelatine solution alters in a notable manner with pH, becoming very small at the iso-electric point. Equation (1) then enables us to see at once why the Tyndall effect becomes very large under the same conditions.

A detailed discussion of colloidal optics on the basis of the thermodynamic theory of light scattering will be published in the *Indian Journal of Physics*.

C. V. RAMAN.

[P6]

APRIL 21, 1928]

No. 3051, VOL. 121] 619

A Change of Wave-length in Light Scattering.

FURTHER observations by Mr. Krishnan and myself on the new kind of light-scattering discovered by us have been made and have led to some very surprising and interesting results.

In order to convince ourselves that the secondary radiation observed by us was a true scattering and not a fluorescence, we proceeded to examine the effect in greater detail. The principal difficulty in observing the effect with gases and vapours was its excessive feebleness. In the case of substances of sufficient light-scattering power, this difficulty was overcome by using an enclosed bulb and heating it up so as to secure an adequate density of vapour. Using a blue-violet filter in the track of the incident light, and a complementary green-yellow filter in front of the observer's eye, the modified scattered radiation was observed with a number of organic vapours, and it was even possible to determine its state of polarisation. It was found that in certain cases, for example,

pentane, it was strongly polarised, while in others, as for example naphthalene, it was only feebly so, the behaviour being parallel to that observed in the liquid state. Liquid carbon dioxide in a steel observation vessel was studied, and exhibited the modified scattering to a notable extent. When a cloud was formed within the vessel by expansion, the modified scattering brightened up at the same time as the ordinary or classical scattering. The conclusion is thus reached that the radiations of altered wave-length from neighbouring molecules are coherent with each other.

A greater surprise was provided by the spectroscopic observations. Using sunlight with a blue filter as the illuminant, the modified scattered radiation was readily detected by the appearance in the spectrum of the scattered light of radiations absent from the incident light. With a suitably chosen filter in the incident light, the classical and modified scatterings appeared as separate regions in the spectrum separated by a dark region. This encouraged us to use a mercury arc as the source of light, all radiations of longer wave-length than 4358 Å. being cut out by a filter. The scattered radiations when examined with a spectroscope showed some sharp bright lines additional to those present in the incident light, their wave-length being longer than 4358 Å.; at least two such lines were prominent and appeared to be accompanied by some fainter lines, and in addition a continuous spectrum. The relation of frequencies between the new lines and those present in the incident light is being investigated by photographing and measuring the spectra. The preliminary visual observations appear to indicate that the position of the principal modified lines is the same for all substances, though their intensity and that of the continuous spectrum does vary with their chemical nature.

C. V. RAMAN.

210 Bowbazar Street,
Calcutta, Mar. 8.

[P7]

MAY 5, 1928]

No. 3053, VOL. 121] 711

The Optical Analogue of the Compton Effect.

THE presence in the light scattered by fluids, of wave-lengths different from those present in the incident light, is shown very clearly by the accompanying photographs (Fig. 1). In the illustration (1) represents the spectrum of the light from a quartz mercury vapour lamp, from which all wave-lengths greater than that of the indigo line have been filtered out. This line (4358 Å.) is marked D in the spectrogram, and C is the group of lines 4047, 4078, and 4109 Å. Spectrogram (2) shows the spectrum of the scattered light, the fluid used being toluene in this case. It will be seen that besides the lines present in the incident spectrum, there are several other lines present in the

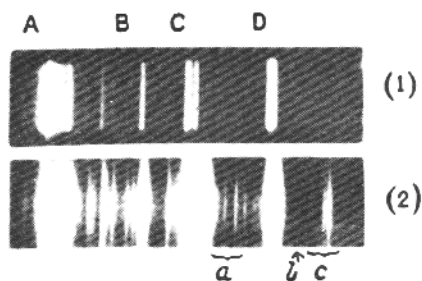


FIG. 1.—(1) Spectrum of incident light; (2) spectrum of scattered light.

scattered spectrum. These are marked *a*, *b*, *c* in the figure, and in addition there is seen visually another group of lines which is of still greater wave-length and lies in a region outside that photographed. When a suitable filter was put in the incident light to cut off the 4358 line, this latter group also disappeared, showing that it derived its origin from the 4358 line in the incident radiation. Similarly, the group marked *c* in spectrogram (2) disappeared when the group of lines 4047, 4078 and 4109 was filtered out from the incident radiation by quinine solution, while the group due to 4358 Å. continued to be seen. Thus the analogy with the Compton effect becomes clear, except that we are dealing with shifts of wave-length far larger than those met with in the X-ray region.

As a tentative explanation of the new spectral lines thus produced by light-scattering, it may be assumed that an incident quantum of radiation may be scattered by the molecules of a fluid either as a whole or in part, in the former case giving the original wave-length, and in the latter case an increased wave-length. This explanation is supported by the fact that the diminution in frequency is of the same order of magnitude as the frequency of the molecular infra-red absorption line. Further, it is found that the shift of wave-length is not quite the same for different molecules, and this supports the explanation suggested.

Careful measurements of wave-length now being made should settle this point definitely at an early date.

C. V. RAMAN.
K. S. KRISHNAN.

210 Bowbazar Street,
Calcutta, Mar. 22.

existence of closed electron orbits of larger than atomic dimensions in association with the crystal lattice.

It may be pointed out that the existence of such orbits appears to furnish a very natural explanation of a variety of phenomena which up to now have been obscure. In the first place, the extremely pronounced diamagnetic anisotropy characteristic of bismuth (and also of graphite) becomes immediately intelligible as a consequence of the specific orientation of the assumed electronic circulations within the crystal lattice. Further, the large Hall effects and changes of electrical resistance exhibited by bismuth and graphite when placed in a magnetic field become comprehensible, since the electronic circulations would be modified by the field, and result in corresponding modifications of the flow of electricity through the substance under a simultaneously impressed electromotive force. There would be every reason to expect, as is indeed the case, that the magnitudes of the Hall effect and the change of resistance would depend on the orientation of the crystal in the magnetic field and the direction of flow of electricity through it.

Then again, with rise of temperature and consequent thermal derangements of the lattice, the postulated electronic circulations would tend to disappear and give place to chaotic electronic movements. The diamagnetic susceptibility would then diminish towards its normal value for a non-crystalline condition of the substance, and corresponding changes would occur in the coefficients of the Hall effect and magnetic variation of electrical resistance. That liquid metals do not, so far as I am aware, exhibit a measurable Hall effect is significant in this connexion.

In close analogy with the influence of temperature, and presumably to be explained on very similar lines, is the remarkable fact that the anomalous diamagnetism of bismuth and of graphite tends to diminish or disappear when the substances are reduced to a colloidal condition.

Finally, it may be remarked that the dimensions of the crystal lattice cannot be uninfluenced by the existence of such regular electronic circulations within it or by modifications produced in them by an external agency. That the magnetostriction of bismuth in strong fields discovered by Dr. Kapitza (*NATURE*, July 13, p. 53) is connected with the anomalous diamagnetism of the substance admits of little doubt. The notable increase in magnetostriction at low temperatures observed by him appears to fit in very well with the Ehrenfest hypothesis.

C. V. RAMAN

[P8]

[SEPTEMBER 14, 1929]

No. 3124, VOL. 124] 412

Anomalous Diamagnetism.

IN a letter in *NATURE* of June 22 (p. 945), reference was made to the Ehrenfest hypothesis which ascribes the high diamagnetic susceptibility of bismuth to the

[P9]

FEB. 5, 1938

No. 3562, VOL. 141 242 243

Light Scattering and Fluid Viscosity

ACCORDING to well-known hydrodynamical theory¹, plane waves of sound propagated through a viscous

liquid suffer a diminution of amplitude in the ratio $1/e$ in traversing a number of wave-lengths given by the quantity $3C\lambda/8\pi^2\nu$, where C is the velocity of sound, λ is the wave-length of sound and ν is the kinematic viscosity. Taking $\lambda = 4358$ Å., this number for various common liquids which are fairly mobile at room temperature ranges from about 3 in the case of butyl alcohol to about 30 in the case of carbon disulphide. For phenol at 25°C ., the number is less than 1, and for glycerine, it is a small fraction of unity. A consideration of these numbers shows that the theories due to Einstein² and L. Brillouin³, which regard the diffusion of light occurring in liquids as due to the reflection of light by regular and infinitely extended trains of sound-waves present in them, can only possess partial validity for ordinary liquids, and must break down completely in the case of very viscous ones. In an earlier note in NATURE⁴, we reported studies of the Fabry-Perot patterns of scattered light with a series of liquids, which showed clearly that the Doppler-shifted components in the spectrum of scattered light fell off in intensity relatively to the undisplaced components, with increasing viscosity of the liquid.

We have now to report some further results which illustrate in a striking way the part played by fluid viscosity in the diffusion of light by liquids. As mentioned in our previous note, the light scattered by liquid phenol at ordinary temperatures gives a Fabry-Perot pattern which is scarcely distinguishable from that of the incident light. When, however, the temperature of the liquid is raised, the viscosity falls off rapidly, and the number $3C\lambda/8\pi^2\nu$ assumes a

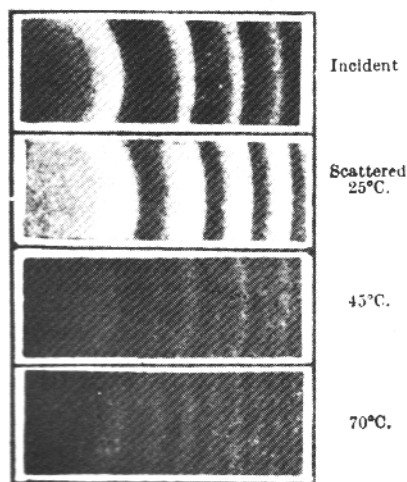


Fig. 1.

INFLUENCE OF TEMPERATURE ON
THE SCATTERING BY PHENOL.

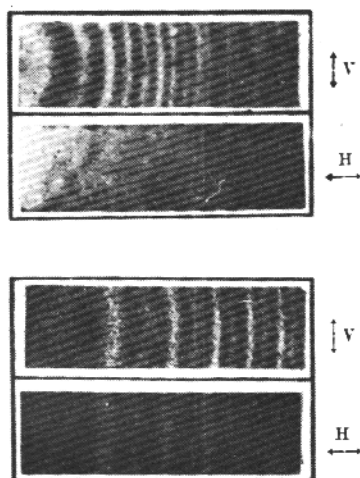


Fig. 2.

STATE OF POLARIZATION; ABOVE,
TOLUENE; BELOW, PHENOL.

value which is many times greater than at room temperature. Simultaneously, as can be seen from Fig. 1, the character of the Fabry-Perot pattern alters, and the Doppler-shifted components come increasingly into evidence; at 70°C they are just as prominent as in ordinary inviscid liquids. The influence of temperature revealed by these studies for the case of the very viscous phenol is to be clearly distinguished from the broadening of the Doppler components with rise of temperature reported by us in an earlier note⁵ for the case of carbon tetrachloride.

The four patterns reproduced in Fig. 2 show the remarkable difference in the state of polarization of the Fabry-Perot patterns of transversely scattered light for an inviscid liquid such as toluene and a viscous one such as phenol at room temperature. In the former case, only a continuous radiation is to be observed in the horizontal component; in other words, both the displaced and the undisplaced components in the pattern are sensibly completely polarized with the vibrations vertical. In the case of phenol, however, the undisplaced radiation is evidently partially polarized, as it appears both in the vertical and the horizontal vibrations; a partial polarization of the continuous radiation is also noticeable.

C. V. RAMAN.

B. V. RAGHAVENDRA RAO.

Department of Physics,
Indian Institute of Science,
Bangalore.
Dec. 29.

¹ Lamb, "Hydrodynamics", fifth edition, p. 613.

² Einstein, A., *Ann. Phys.*, **33**, 1275 (1910).

³ Brillouin, L., *Ann. Phys.*, **17**, 88 (1922).

⁴ NATURE, **139**, 585 (April 3, 1937).

⁵ NATURE, **135**, 761 (May 4, 1935).

[P10]

JAN. 27, 1940

No. 3665, Vol. 145 147

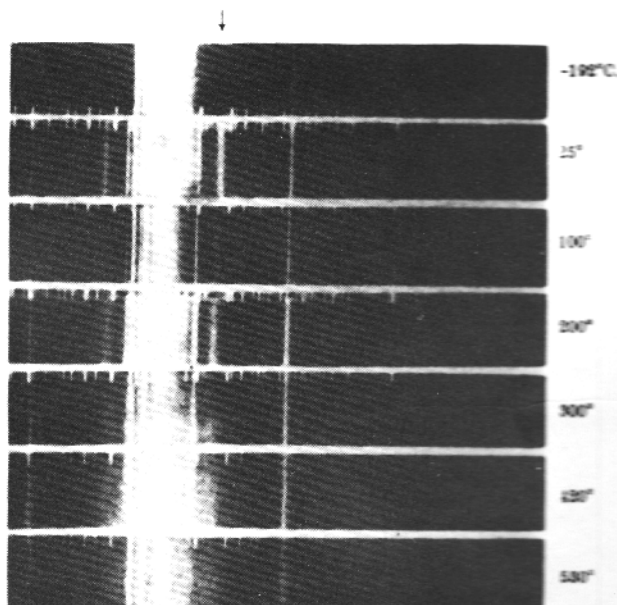
The α - β Transformation of Quartz

As is well known, the ordinary form of quartz which has trigonal symmetry changes over reversibly to another form which has hexagonal symmetry at a temperature of 575°C. Though the transformation does not involve any radical reorganization of the internal architecture¹ of the crystal and takes place at a sharply defined temperature, it is nevertheless preceded over a considerable range of temperature (200°-575°) by a progressive change in the physical properties of 'low' quartz which prepares the way for a further sudden change, when the transition to 'high' quartz actually takes place. The thermal expansion coefficients, for example, gradually increase over this range of temperature, becoming practically infinite at the transition point and then suddenly dropping to small negative values². Young's moduli in the same temperature range fall to rather low values at the transition point and then rise sharply to high figures³. The piezo-electric activity also undergoes notable changes^{4,5}.

In the hope of obtaining an insight into these remarkable phenomena, a careful study has been made of the spectrum of monochromatic light scattered in a quartz crystal at a series of temperatures ranging from that of liquid air to nearly the transition point. Significant changes are observed which are illustrated in the accompanying illustration, reproducing part of the spectrum excited by the 4358 Å. radiation of the mercury arc. A fully exposed spectrum at room temperature indicates fourteen different normal modes of vibration of the crystal. At liquid air temperature, the three most intense lines correspond to the frequency shifts 132, 220 and 468 cm.⁻¹ and are all about equally sharp. As the crystal is heated over the temperature range 200°-530°, notable changes occur. The 220 cm.⁻¹ line (marked with an arrow in the reproduction) behaves in an exceptional way, spreading out greatly towards the exciting line and becoming a weak diffuse band

as the transition temperature is approached. On the other hand, the other intense lines having both larger and smaller frequency shifts continue to be easily visible, though appreciably broadened and displaced.

The behaviour of the 220 cm.⁻¹ line clearly indicates that the binding forces which determine the frequency of the corresponding mode of vibration of the crystal lattices diminish rapidly with rising temperature. It appears therefore reasonable to infer that the increasing excitation of this particular mode of vibration with rising temperature and the deforma-



LIGHT SCATTERING IN QUARTZ.

tions of the atomic arrangement resulting therefrom are in a special measure responsible for the remarkable changes in the properties of the crystal already mentioned, as well as for inducing the transformation from the α to the β form.

C. V. RAMAN.

T. M. K. NEDUNGIADI.

Department of Physics,
Indian Institute of Science,
Bangalore.
Dec. 11.

¹ Bragg and Gibbs, *Proc. Roy. Soc., A*, **106**, 405 (1925).

² Jay, *Proc. Roy. Soc., A*, **142**, 237 (1933).

³ Perrier and Mandrot, *C.R.*, **175**, 622 (1922).

⁴ Osterberg and Cookson, *J. Frank. Inst.*, **220**, 361 (1935).

⁵ Pitt and McKinley, *Canad. J. Res.*, **A**, **14**, 58 (1936).

[P11]

Journal of the Optical Society of America and Review of Scientific Instruments

Vol. 15

OCTOBER, 1927

Number 4

THE SCATTERING OF LIGHT IN AMORPHOUS SOLIDS

By C. V. RAMAN

1. INTRODUCTION

Recent investigations have shown that when light traverses a dust-free liquid, an observable fraction of the energy is laterally scattered and that this effect is due to the local fluctuations of density and to the random orientations of the molecules which cause the fluid to be optically inhomogeneous.¹ In the case of a mixture of liquids, we have in addition a scattering due to the local fluctuations of composition which cause corresponding local variations of refractive index. Since the transverse scatterings due to density and composition fluctuations are fully polarized, while that due to the random orientation of the molecules is almost entirely unpolarized, the resultant scattering in a fluid is usually only partially polarized. When the temperature of a liquid is lowered, its compressibility usually diminishes and with it also the local fluctuations of density. Thus we may expect that when the liquid is cooled to such an extent that it passes into the amorphous solid condition, the density scattering would become very small. On the other hand, in liquid mixtures, the local fluctuations of *composition* usually tend to increase rather than to diminish with fall of temperature. Thus they should certainly tend to persist or even increase when the mixture congeals into an amorphous solid. The effect due to random molecular orientations would certainly remain in the amorphous solid condition. Thus, we may anticipate that an amorphous solid such as glass consisting of a mixture of anisotropic molecules would exhibit when light traverses it, a partially-polarized internal scattering or opalescence of an order of intensity not greatly inferior to that ordinarily observed in liquids or liquid mixtures.

¹ C. V. Raman, *Molecular Diffraction of Light*, Calcutta University Press, 1922.

An internal scattering of light in common glasses and also in optical glasses has actually been noticed.² Its nature has been a subject of debate,³ and owing to our insufficient knowledge of the amorphous state, is not fully understood at present. Judging, however, from such observations as are available, it is the opinion of the writer, that the effect observed in optical glasses is a true molecular scattering arising from local fluctuations of composition and of molecular orientation, being thus of the same general nature as the opalescence observed in binary liquid mixtures such as phenol-water, carbon disulphide-methyl alcohol and so on. In support of this view, it is proposed in this paper to give the results of the study of the light-scattering in a series of 14 different optical glasses manufactured by the firm of Schott in Jena.⁴ If the light-scattering in glass were due to accidental inclusions or incipient crystallizations occurring within it as has been suggested by some writers, we should expect the intensity of the scattered light to show large and arbitrary variations depending on the circumstances of the particular melting from which the specimen was taken. On the other hand, if the phenomenon has a true molecular origin, we should expect to find the intensity of scattering to be definitely correlated with the refractivity and chemical constitution of the glass.

TABLE 1. *List of classes examined.*

	Melting	Type	Composition	Refractive index μ	$\nu = 1/\omega$
No. 1	18165	0.6781	Fluor crown	1.4933	69.9
2	4927	U. V. 3199	U. V. crown	1.5035	64.4
3	15189	0.144	Borosilicate crown	1.5100	64
4	16564	0.3832	Prism crown	1.5163	64
5	15065	0.3453	Silicate crown	1.5191	60.4
6	16740	0.3439	Telescopic flint	1.5286	51.6
7	16397	0.7550	Baryta light flint	1.5694	56
8	14657	0.211	Densest Borosilicate crown	1.5726	57.5
9	17538	0.340	Ordinary Light flint	1.5774	41.4
10	18023	0.1266	Baryta light flint	1.6042	43.8
11	11095	0.103	Ordinary flint	1.6202	36.2
12	10259	0.748	Baryta flint	1.6235	39.1
13	8988	0.102	Dense flint	1.6489	33.8
14	16889	0.198	Densest flint	1.7782	26.5

² Lord Rayleigh, *Proc. Roy. Soc.*, 95, p. 476, 1919, and C. V. Raman, "Molecular Diffraction of Light," p. 85.

³ R. Gans, *Ann. der Phys.*, 77, p. 317; 1925.

⁴ The specimens were presented by Messrs. Schott to Prof. P. N. Ghosh, who kindly placed them at the writer's disposal for the work.

2. THE SPECIMENS EXAMINED

Table 1 gives a list of the glasses examined and their description as furnished by the manufacturers, arranged in order of increasing refractive index. The samples were furnished in the form of slabs 7 cm \times 7 cm \times 2 cm, with one pair of end-faces polished. For the purpose of the observation of light-scattering, the slabs were immersed in a trough containing benzene and a beam of sunlight focused by a lens was admitted through a side-face, the necessity of polishing the latter being thus avoided. The track of the beam as seen through the end-faces was perfectly uniform and appeared of a beautiful sky-blue color.

3. EXPERIMENTAL RESULTS

When the scattered light was viewed through a double-image prism held so that the direction of vibrations in the two images seen were respectively perpendicular and parallel to the direction of the beam traversing the glass, it was seen that these were of very different intensities, showing that the scattered light was strongly but not completely polarized. The color of the stronger image was always a sky-blue. The color of the fainter image in the ordinary flint glasses was blue, but in the other specimens varied very considerably. The total intensity of the scattered light in the glasses was determined by comparison with that of the track in a bulb containing dust-free benzene immersed in the same trough as the block of glass under examination and traversed by the same beam of light. A rotating-sector photometer was used for the purpose. The ratio of the intensities in the parallel and perpendicular components of vibration in the laterally scattered light was also determined with the help of a double-image prism and nicol (Cornu's method) in the usual way. The measurements give us the ratio of the intensity of the faint image to the bright image seen through the double image prism, and this expresses the degree of depolarization of the scattered light.

The results of the work are gathered together in Table 2.

4. DISCUSSION OF RESULTS

From a scrutiny of the figures in Table 2, several interesting facts emerge. In the first place, it will be seen that the crown glasses show uniformly a smaller intensity of light-scattering than the other varieties of glass. Both the ordinary flints and the baryta flints scatter light strongly, the latter more so than ordinary flints of equal refractive index. It will be seen also that considering each species of glass sepa-

rately, there is a progressive increase of the intensity of light-scattering with increasing refractive-index. The colors shown by the fainter components of the scattered light in the first four glasses in Table 2 are obviously due to a species of weak fluorescence, probably of the same kind as has been met with in investigations on light-scattering in liquids.* This fluorescence being unpolarized, the large values of the depolarization found in the case of these glasses stands self-explained. If the fluorescent light had been excluded by the introduction of

TABLE 2. *Experimental results.*

	Glass	Refractive index	Color of bright component	Color of faint component	Depolarization	Intensity relative to benzene = 1
No. 1	Fluor crown	1.4933	Blue	Yellow	0.180	0.18
2	U. V. crown	1.5035	"	Pink	0.158	0.12
3	Borosilicate crown	1.5100	"	"	0.295	0.11
4	Prism crown	1.5163	"	"	0.285	0.14
5	Silicate crown	1.5191	"	Blue	0.123	0.18
6	Telescopic flint	1.5286	"	Purple	0.068	0.40
7	Baryta light flint	1.5694	"	"	0.053	0.44
8	Densest borosilicate crown	1.5726	"	"	0.045	0.37
9	Ordinary light flint	1.5774	"	Indigo-blue	0.067	0.30
10	Baryta light flint	1.6042	"	Indigo	0.067	0.41
11	Ordinary flint	1.6202	"	Blue	0.079	0.42
12	Baryta flint	1.6235	"	Indigo-blue	0.085	0.57
13	Dense flint	1.6489	"	Blue	0.062	0.52
14	Densest flint	1.7782	"	"	0.065	0.63

suitable color-filters, the depolarization for these glasses would have been much smaller. It is interesting to notice that in glasses Nos. 6, 7, and 8, we have a low value for the depolarization in spite of the obvious presence of a weak fluorescence; this is obviously due to the greater intensity of polarized scattering appearing in the last column of Table 2 of these glasses.

The several regularities to which attention has been drawn above, particularly the fact that the intensity of scattering is very clearly a function of the refractive-index and chemical composition of the glass, render it extremely improbable that the effect can arise from accidental inclusions or imperfections in the structure of the glasses. It is, in fact, clear from the data that the effect arises from the ultimate molecular structure of glass.

* K. S. Krishnan, *Phil. Mag.*, 50, p. 697; 1925.

It would be very interesting to study the light-scattering in amorphous solids having a relatively simple chemical constitution, e.g., transparent quartz-glass. Experiments on the scattering of light in liquids which can first be rendered dust-free and then supercooled into the amorphous solid state may also be expected to furnish important information. Further work on these lines is in progress.

210 BOWBAZAR STREET,
CALCUTTA, INDIA,
MAY 11, 1927.

A New Radiation¹

BY

PROF. C. V. RAMAN, F.R.S.

(Plate XII).

1. *Introduction.*

I propose this evening to speak to you on a new kind of radiation or light-emission from atoms and molecules. To make the significance of the discovery clear, I propose to place before you the history of the investigations made at Calcutta which led up to it. Before doing so, however, a few preliminary remarks regarding radiation from atoms and molecules will not be out of place.

Various ways are known to the physicist by which atoms or molecules may be caused to emit light, as for instance, heating a substance or bombarding it with a stream of electrons. The light thus emitted is usually characteristic of the atoms or molecules and is referred to as *primary* radiation. It is also possible to induce radiation from atoms and molecules by illuminating them strongly. Such light-emission is referred to as *secondary* radiation. The familiar diffusion of light by rough surfaces may be cited as an example of secondary radiation, but strictly speaking, it hardly deserves the name, being an effect occurring at the boundaries between media of different refractive indices and not a true volume-effect in which all the atoms and molecules of the substance

¹ Inaugural Address delivered to the South Indian Science Association on Friday, the 16th March, 1928, at Bangalore.

RAMAN

PLATE XII

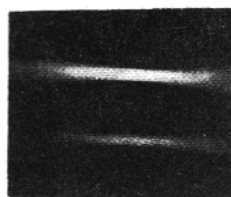


Fig. 1

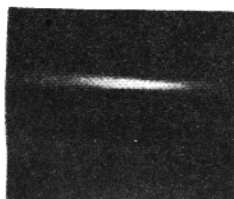
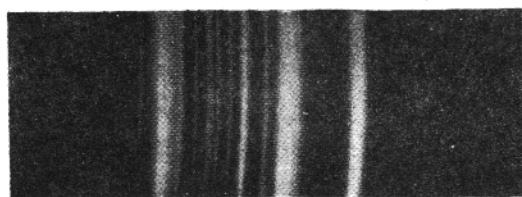
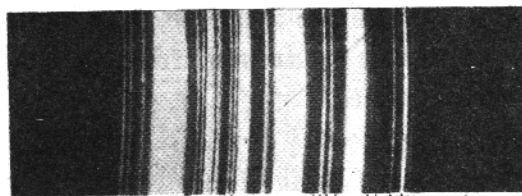
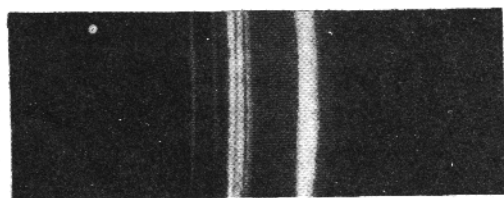
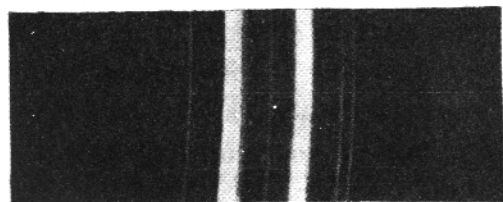


Fig. 2.

Fig 3 (1)
Incident SpectrumFig 3 (2)
Scattered SpectrumFig 4 (1)
Incident SpectrumFig 4 (2)
Scattered Spectrum

take part. The first case discovered of secondary radiation really worthy of the name was the phenomenon of fluorescence whose laws were elucidated by the investigations of Sir George Stokes. This is a familiar effect which is exhibited in a very conspicuous manner in the visible region of the spectrum by various organic dye-stuffs. I have here a bottle of water in which an extremely small quantity of fluorescein is dissolved. You notice that when placed in the beam of light from the lantern, it shines with a vivid green light, and that the colour of the emission is not altered, though its brightness is changed, by placing filters of various colours between the bottle and the lantern. A violet filter excites the green fluorescence strongly, while a red filter has but little effect.

Another kind of secondary radiation whose existence has been experimentally recognized more recently is the scattering of light by atoms and molecules. It is this scattering that gives us the light of the sky, the blue colour of the deep sea and the delicate opalescence of large masses of clear ice. I have here a large bottle of a very clear and transparent liquid, toluene, which as you notice contains hardly any dust-particles, but the track of the beam from the lantern passing through it is visible as a brilliant blue cone of light. This internal opalescence continues to be visible even after the most careful purification of the liquid by repeated distillation in vacuo. A similar opalescence is shown, though much less brightly, by dust-free gases and vapours, and also by solids. A large clear block of ice shows a blue colour in the track of the beam when sunlight passes through it. The blue opalescence of blocks of clear optical glass is also readily demonstrable. The molecular scattering of light is thus a phenomenon common to all states of matter.

During the past seven years, the scattering of light in transparent media has been the subject of intensive experimental and theoretical investigation at Calcutta, and it is the

researches made on this subject that have led to the discovery which I shall lay before you this evening. One important outcome of our researches has been to show that while light-scattering is in one sense a molecular phenomenon, in another sense it is a bulk-effect having a thermal origin. It is the thermal agitation of the molecules which causes them to be distributed and orientated in space with incomplete regularity, and it is the local fluctuations in the properties of the medium thus arising which give rise to optical heterogeneity and consequent diffusion of light. The subject of light-scattering is thus a meeting ground for thermodynamics, molecular physics and the wave-theory of radiation. That the combination of theories in such diverse fields of physics gives us predictions which have been experimentally verified, is one of the triumphs of modern physics.

2. *A New Phenomenon.*

While the quantitative investigations made at Calcutta have in the main substantiated the thermodynamic-wave-optical theory of light-scattering, indications appeared even in our earliest studies of a new phenomenon which refused to fit in with our pre-conceived notions. Thus, in some observations made by me¹ with the assistance of Mr. Seshagiri Rao in December, 1921, it was found that the depolarisation of the light transversely scattered by distilled water measured with a double-image prism and Nicol increased very markedly when a violet filter was placed in the path of the incident light. More careful investigations made with dust-free liquids² in 1922, confirmed this effect and showed it to exist also in methyl and ethyl alcohols, and to a lesser degree in ether. It was also noticed that the colours of the scattered light from the different liquids studied did not match

¹ "Molecular Diffraction of Light," Calcutta University Press, February, 1922.

² C. V. Raman and K. S. Rao, *Phil. Mag.*, Vol. 45, p. 633, 1923.

perfectly. An important advance was made when Dr. Ramanathan¹ working at Calcutta in the summer of 1923, investigated the phenomenon more closely and discovered that it was not a true dependance of the depolarisation on the wave-length of the scattering radiation but was due to the presence in the scattered light of what he described as "a trace of fluorescence." This was shown by the fact that the measured depolarisation depended on whether the blue filter used was placed in the path of the incident beam or of the scattered light, being smaller in the latter case. Accepting the explanation of the effect as "weak fluorescence," it naturally became important to discover whether it was due to some impurity present in the substance. Dr. Ramanathan tested this by careful chemical purification followed by repeated slow distillation of the liquid at the temperature of melting ice. He found that the effect persisted undiminished.

The investigation of this species of "weak fluorescence" has ever since 1923 been on our programme of research at Calcutta. Krishnan,² who investigated 60 liquids for light-scattering in the spring and summer of 1924, made systematic studies of the phenomenon, and found that it was shown markedly by water, ether, all the monohydric alcohols and a few other compounds. He pointed out that the liquids which exhibit the effect have certain family relationships amongst themselves, and that they are also substances whose molecules are known to be polar. The chemical importance of the subject led to Mr. S. Venkateswaran attempting to make a fuller study of it in the summer of 1925, but without any special success. The research was discontinued at the time but was resumed by him later in the current year (January, 1928). The remarkable observation was made that the visible radiation which is excited

¹ K. R. Ramanathan, *Proc. Ind. Assoc. Cultn. Science*, Vol. VIII, p. 190, 1923.

² K. S. Krishnan, *Phil. Mag.*, Vol. L, p. 697, 1925.

in pure dry glycerine by ultra-violet radiation (sunlight filtered through Corning glass G. 586) *is strongly polarised*.

The possibility of a similar effect in gases and vapours was also borne in mind and repeatedly looked for by the workers at Calcutta. The feebleness of the scattering in gases and vapours, and the infructuousness of the earlier efforts in this direction, however discouraged progress.

3. *Its Universality.*

Though the phenomenon was described in the paper of Dr. Ramanathan and Mr. Krishnan as a "feeble fluorescence," the impression left on my mind at the time was that we had here an entirely new type of secondary radiation distinct from what is usually described as fluorescence. The publication of the idea was however discouraged by the belief then entertained that only a few liquids exhibited the effect and by the supposition that it was unpolarised in the same way as ordinary fluorescence in liquids. Indeed, a chemical critic might even have asserted that the effect was in each case due to a trace of dissolved fluorescent impurity present in the substance which our efforts at purification had failed to remove. Early this year, however, a powerful impetus to further research was provided when I conceived the idea that the effect was some kind of optical analogue to the type of X-ray scattering discovered by Prof. Compton, for which he recently received the Nobel Prize in Physics. I immediately undertook an experimental re-examination of the subject in collaboration with Mr. K.S. Krishnan and this has proved very fruitful in results. The first step taken in the research was to find whether the effect is shown by all liquids. The method of investigation was to use a powerful beam of sunlight from a heliostat concentrated by a 7" telescope objective combined with a short focus lens. This was passed through a blue-violet filter and then through the liquid under examination contained in

an evacuated bulb and purified by repeated distillation in vacuo. A second filter of green glass was used which was complementary in colour to the blue-violet filter. If it were placed in the track of the incident light, all illumination disappears, while, if it be placed between the bulb and the observer's eye, the opalescent track within the liquid continued to be visible, though less brightly. All the liquids examined (and they were some 80 in number) showed the effect in a striking manner. There was therefore no longer any doubt that the phenomenon was universal in character; with the bulb of toluene on the lantern, you see that the effect is readily demonstrable. The cone of light vanishes when I place the violet and green filters together, but it appears when I transfer the latter to a place between my audience and the observation bulb.

Now the test with the complementary filters is precisely that ordinarily used for detecting fluorescence and indeed was first suggested by Stokes in his investigations on the subject. You may therefore rightly ask me the question how does this phenomenon differ from fluorescence? The answer to the question is, firstly, that it is of an entirely different order of intensity. A more satisfactory proof was however forthcoming when Mr. Krishnan and myself examined the polarisation of this new type of radiation and found that it was nearly as strong as that of the ordinary light scattering in many cases, and is thus quite distinct from ordinary fluorescence which is usually unpolarised.

This is shown for the case of toluene in Figs. 1 and 2 in Plate XII. Fig. 1 is a photograph of the scattering by toluene of sunlight filtered through a blue-violet glass. It was taken through a double-image prism of iceland spar with an exposure of 3 seconds. Fig. 2 is a picture with an additional complementary filter of green glass interposed in front of the camera lens. The exposure necessary is now increased greatly by the insensitiveness of the plate to green light, and

had to be as much as 25 minutes. It will be noticed that the polarisation of the track as shown by the difference in brightness of the two polarised images is quite as prominent in Fig. 2 as in Fig. 1.

I may also mention that Mr. Krishnan and myself have succeeded in detecting the new radiation and observing its partial polarisation in a number of organic vapours and also in the gases CO_2 and N_2O . The problem in these cases is one of securing sufficient intensity of scattering for the effect to be detectable through the complementary filter. This can be secured by heating up the substance in a sealed bulb or by using steel observation-vessels for containing the compressed gases, so as to obtain sufficient density of the scattering molecules. The question of the background against which the track is observed is also of great importance.

The new type of secondary radiation is also observable in crystals such as ice, and in amorphous solids. It is thus a phenomenon whose universal nature has to be recognised.

4. *Line-Spectrum of New Radiation.*

That the secondary radiation passes the complementary filter and yet is strongly polarised to an extent comparable with the ordinary molecular scattering, is clear evidence that we have in it an entirely new type of secondary radiation which is distinct from either the ordinary scattering or the usual type of fluorescence. A striking and even startling confirmation of this view is furnished by an examination of its spectrum. Preliminary observations with sunlight filtered through a combination which passes a narrow range of wave-lengths, showed the spectrum of the new radiation to consist mainly of a narrow range of wave-lengths clearly separated from the incident spectrum by a dark space. This encouraged me to take up observations with a monochromatic source of light. A quartz mercury lamp with a filter which completely

cuts out all the visible lines of longer wave-length than the indigo line 4,358. A. U. was found to be very effective. When the light from such a lamp was passed through the bulb containing a dust-free liquid, and the spectrum of the scattered light was observed through a direct-vision spectroscope, it was found to exhibit two or more sharp bright lines in the blue and green regions of the spectrum. These lines are not present in the spectrum of the incident light or in the unfiltered light of the mercury arc and are thus manufactured by the molecules of the liquid.

Figs. 3 (1) and 3 (2), and Figs. 4 (1) and 4 (2) show the phenomenon. They are spectrograms taken with a small Hilger quartz instrument of the scattering by *liquid* benzene. Fig. 3 was taken with the light from the quartz mercury arc filtered through a blue glass which allows the wave-lengths from about 3,500 A. U. to 4,400 A. U. to pass through. Fig. 3 (1) represents the incident-spectrum and Fig. 3 (2) the scattered spectrum, and the latter shows a number of sharp lines not present in Fig. 3 (1). These are indicated in the figure. Figs. 4 (1) and (2) similarly represent the incident and scattered spectra with benzene liquid, the filter used being a potassium permanganate solution. Here again the new lines which appear are indicated in the figure. Visual observations were also made using a quinine sulphate solution together with the blue glass as a filter and thus cutting off all the radiations except 4,358 A.U. from the incident spectrum. Some of the modified lines then disappear, leaving only those of longer wave-length. It is thus clear that each line in the incident spectrum gives rise to at least two lines in the scattered spectrum, one in the original or unmodified position, and a second in a shifted position of longer wave-length. There is thus a striking analogy with the Compton effect in the X-ray region.

There has, as yet, not been sufficient time for photographing the spectra from a large number of liquids, or even for measuring the photographs already obtained. Visual obser-

variations have however been made with a large number of liquids. There is an astonishing similarity between the spectra obtained with different liquids. When only the 4,358 line was used, most liquids showed in the spectrum of the scattered light, a bright line in the blue-green region of the spectrum (about 5,000 A.U.), whose position was practically the same for chemically similar liquids such as pentane, hexane and octane for instance. There was, however, a recognizable difference in the position of the modified line when other liquids such as benzene or water were used. When the 4,047 line of the mercury arc was let in by removing the quinine sulphate solution, a second modified line in the blue region of the spectrum was seen with most liquids.

Photographs obtained so far with benzene and toluene suggest that there may be several modified lines, and that each modified line may be a doublet in some cases. In many liquids, the scattered spectrum shows in addition to sharp lines also an unmistakable continuous spectrum accompanying it. Carbon disulphide behaves in an exceptional manner, showing a diffuse band.

Observations already made show that the new lines in the scattered spectrum are usually markedly polarised; they also suggest that a continuous spectrum, when present, is less markedly polarised.

5. *Nature of the New Radiation.*

The discovery set out above naturally opens up an array of problems for investigation. The most pressing question is, how is the modified scattered radiation, as we may call it, generated by the molecules of the liquid? As a tentative explanation, we may adopt the language of the quantum theory, and say that the incident quantum of radiation is partially absorbed by the molecule, and that the unabsorbed part is scattered. The suggestion does not seem to be altogether

absurd and indeed such a possibility is already contemplated in the Kramers-Heisenberg theory of dispersion. If we accept the idea indicated above, then the difference between the incident and scattered quanta would correspond to a quantum of absorption by the molecule. The measurement of the frequencies of the new spectral lines thus opens a new pathway of research into molecular spectra, particularly those in the infra-red region.

If a molecule can take up part of the incident quantum of radiation and scatter the remaining part, then it might also be capable of adding a quantum of its own characteristic frequency to the incident radiation when scattering it. In such a case we should expect a modified line of *increased* frequency. Such a result appears to be shown in Fig. 3 (2) of Plate XII, as a solitary line in the extreme left of the photograph. This result, however, requires to be confirmed by more photographs and with other liquids. So far it would appear that a degradation of frequency is more probable than an enhancement. It is too early to speculate at present on the origin of the continuous radiation observed in some cases, whether it is due to changes in the molecule itself, or whether it arises from inelastic collisions of the second kind within the liquid resulting in *partial* transformation of the incident quantum of radiation into translatory kinetic energy of the molecules. When further data are obtained, it should be possible to express a definite opinion on this point, and also on the role played by the solvent in the explanation of ordinary fluorescence.

6. *Relation to Thermodynamics.*

As explained in the introduction, the ordinary scattering of light can be regarded equally well as a molecular effect, and as a bulk effect arising from the thermodynamic fluctuations of the whole medium. The question arises whether the

new type of secondary radiation is exclusively a molecular effect or not, and whether it is related in any way to thermodynamics. The question is obviously one to be answered by experiment and theory conjointly. The comparative study of the effect at different temperatures and in different states of aggregation of matter is obviously of great importance in this connection. It has already been remarked that the effect is observable in gases and vapours and indeed it is found possible to determine its intensity and polarisation in the gaseous state. It is also of great interest to remark that the solid crystal ice also shows the sharp modified lines in the scattered spectrum in approximately the same positions as pure water. The only observations made with amorphous solids are with optical glass. Here the modified scattered spectrum consists of diffuse bands and not sharp lines. Whether this is generally true for all amorphous solids, and whether any changes occur at low and high temperatures remains to be determined by experiment.

7. *Coherent or Non-Coherent Radiation?*

An important question to be decided in the first instance by experiment is whether the modified scattered radiations from the different molecules are incoherent with each other. One is tempted to assume that this must be the case, but a somewhat astonishing observation made with liquid carbon dioxide contained in steel observation vessels gives us pause here. It was found on blowing off the CO_2 by opening a stop-cock, a cloud formed within the vessels which scattered light strongly in the ordinary way. On viewing the cloud through the complementary filter, the scattered radiation of modified frequency also brightened up greatly. This would suggest that the assumption of non-coherence is unjustifiable. Further, some qualitative observations suggest that the modified scattering by a mixture of carbon disulphide and methyl alcohol also brightens up notably at the critical

solution temperature. Quantitative observations are necessary to decide the very fundamental question here raised.

8. *Possible X-Ray Analogies.*

If a quantum of radiation can be absorbed in part and scattered in part in the optical region of the spectrum, should not similar phenomena also occur in X-ray scattering? The type of scattering discovered by Prof. Compton may possibly be only one of numerous other types of scattering with modified frequencies, some with a line spectrum and some in the nature of continuous radiation. The extreme ultra-violet region of the spectrum may also furnish us with numerous examples of the new type of radiation, which clearly occupies a position intermediate between scattering and fluorescence.

9. *Conclusion.*

We are obviously only at the fringe of a fascinating new region of experimental research which promises to throw light on diverse problems relating to radiation and wave-theory, X-ray optics, atomic and molecular spectra, fluorescence and scattering, thermodynamics and chemistry. It all remains to be worked out.

I have to add in conclusion that I owe much to the valuable co-operation in this research of Mr. K. S. Krishnan, and the assistance of Mr. S. Venkateswaran and other workers in my laboratory.

The line spectrum of the new radiation was first seen on the 28th February, 1928. The observation was given publicity the following day.

(Issued separately, 31st March, 1928).

[P13]

THE DIFFRACTION OF LIGHT BY HIGH FREQUENCY SOUND WAVES : PART I.

BY C. V. RAMAN

AND

N. S. NAGENDRA NATH.

(From the Department of Physics, Indian Institute of Science, Bangalore.)

Received September 28, 1935.

1. Introduction.

As is well known, Langevin showed that high frequency sound-waves of great intensity can be generated in fluids by the use of piezo-electric oscillators of quartz. Recently, Debye and Sears¹ in America and Lucas and Biquard² in France have described very beautiful experiments illustrating the diffraction of light by such high-frequency sound-waves in a liquid. Amongst the experimenters in this new field, may be specially mentioned R. Bär³ of Zürich who has carried out a thorough investigation and has published some beautiful photographs of the effect. The arrangement may be described briefly as follows. A plane beam of monochromatic light emerging from a distant slit and a collimating lens is incident normally on a cell of rectangular cross-section and after passing through the medium emerges from the opposite side. Under these conditions, the incident beam will be undeviated if the medium be homogeneous and isotropic. If, however, the medium be traversed by high-frequency sound-waves generated by introducing a quartz oscillator at the top of the cell, the medium becomes stratified into parallel layers of varying refractive index. Considering the case in which the incident beam is parallel to the plane of the sound-waves, the emerging light from the medium will now consist of various beams travelling in different directions. If the inclination of a beam with the incident light be denoted by θ , it has been found experimentally that the formula

$$\sin \theta = \pm \frac{n\lambda}{\lambda^*}, \quad n \text{ (an integer)} \geq 0 \quad (1)$$

is in satisfactory agreement with the observed results, where λ and λ^* are the wave-lengths of the incident light and the sound wave in the medium

¹ P. Debye and F. W. Sears, *Proc. Nat. Acad. Sci. (Washington)*, 1932, 18, 409.

² R. Lucas and P. Biquard, *Jour. de Phys. et Rad.*, 1932, 3, 464.

³ R. Bär, *Helv. Phys. Acta*, 1933, 6, 570.

Diffraction of Light by High Frequency Sound Waves—I 407

respectively. With sound waves of sufficient intensity, numerous orders of these diffraction spectra have been obtained; a wandering of the intensity amongst these orders has also been noticed by Bär³ when the experimental conditions are varied.

Various theories of the phenomena have been put forward by Debye and Sears,¹ by Brillouin,⁴ and by Lucas and Biquard.² The former have not presented quantitative results and it is hard to understand from their theory as to why there should be so many orders and why the intensity should wander between the various orders under varying experimental conditions. In Brillouin's theory, the phenomenon is attributed to the reflection of light from striations of the medium caused by the sound waves. We know, however, from the work of Rayleigh that the reflection of light by a medium of varying refractive index is negligible if the variation is gradual compared with the wave-length of light. Under extreme conditions, we might perhaps obtain the Brillouin phenomenon, but the components of reflection should be very weak in intensity compared to the transmitted ones. As one can see later on in this paper, the whole phenomenon including the positions of the diffracted beams and their intensities can be explained by a simple consideration of the transmission of the light beam in the medium. Lucas and Biquard attribute the phenomenon to an effect of mirage of light waves in the medium. In what way the relation (1) enters in their theory is not clear. The wandering of the intensities of the various components observed by Bär has not found explanation in any of the above theories.

We propose in this paper a theory of the phenomenon on the simple consideration of the regular transmission of light in the medium and the phase changes accompanying it. The treatment is limited to the case of normal incidence. The formula (1) has been established in our theory. Also, a formula for the intensities of the various components has been derived. It is found that the above results are in conformity with the experimental results of Bär.³

2. *Diffraction of light from a corrugated wave-front.*

The following theory bears a very close analogy to the theory of the diffraction of a plane wave (optical or acoustical) incident normally on a periodically corrugated surface, developed by the late Lord Rayleigh.⁵ He showed therein that a diffraction phenomenon would ensue in which the positions of the various components are given by a formula similar to (1)

⁴ L. Brillouin, "La Diffraction de la Lumière par des Ultra-sons", *Act. Sci. et Ind.*, 1933, 59.

⁵ Lord Rayleigh, *Theory of Sound* (Vol. 2), page 89.

and their relative intensities are given by a formula similar to the one we have found.

Consider a beam of light with a plane wave-front emerging from a rectangular slit and falling normally on a plane face of a medium with a rectangular cross-section and emerging from the opposite face parallel to the former. If the medium has the same refractive index at all its points, the incident beam will emerge from the opposite face with its direction unchanged. Suppose we now create layers of varying refractive index in the medium, say by suitably placing a quartz oscillator in the fluid. If the distance between the two faces be small, the incident light could be regarded as arriving at the opposite face with variations in the phase at its different parts corresponding to the refractive index at different parts of the medium. The change in the phase of the emerging light at any of its parts could be simply calculated from the optical lengths found by multiplying the distance between the faces and the refractive index of the medium in that region. This step is justified for $\int \mu(x, y, z) ds$ taken over the actual path is minimum, *i.e.*, it differs from the one taken over a slightly varied hypothetical path by a differential of the second order. So, the incident wave-front becomes a periodic corrugated wave-front when it traverses a medium which has a periodic variation in its refractive index. The origin of the axes of reference is chosen at the centre of the incident beam projected on the emerging face, the boundaries of the incident beam being assumed to be parallel to the boundaries of the face. The X-axis is perpendicular to the sound-waves and the Z-axis is along the direction of the incident beam of light. If the incident wave is given by

$$Ae^{2\pi i \nu t}$$

it will be

$$Ae^{2\pi i \nu \{t - L\mu(x)/c\}}$$

when it arrives at the other face where L is the distance between the two faces and $\mu(x)$ the refractive index of the medium at a height x from the origin. It is assumed that the radii of curvature of the corrugated wave-front are large compared with the distance between the two faces of the cell. If μ_0 be the refractive index of the whole medium in its undisturbed state, we can write $\mu(x)$ as given by the equation

$$\mu(x) = \mu_0 - \mu \sin \frac{2\pi x}{\lambda^*}$$

ignoring its time variation, μ being the *maximum variation* of the refractive index from μ_0 .

The amplitude due to the corrugated wave at a point on a distant screen parallel to the face of the medium from which light is emerging whose join

Diffraction of Light by High Frequency Sound Waves—I 409

with the origin has its x -direction-cosine l , depends on the evaluation of the diffraction integral

$$\int_{-p/2}^{p/2} e^{2\pi i \{lx + \mu L \sin(2\pi x/\lambda^*)\}} / \lambda \, dx$$

where p is the length of the beam along the X -axis. The real and the imaginary parts of the integral are

$$\int_{-p/2}^{p/2} \{\cos ulx \cos(v \sin bx) - \sin ulx \sin(v \sin bx)\} dx$$

and

$$\int_{-p/2}^{p/2} \{\sin ulx \cos(v \sin bx) + \cos ulx \sin(v \sin bx)\} dx$$

where $u = 2\pi/\lambda$, $b = 2\pi/\lambda^*$ and $v = u\mu L = 2\pi\mu L/\lambda$.

We need the well-known expansions

$$\cos(v \sin bx) = 2 \sum_0^{\infty} J_{2r} \cos 2rbx$$

$$\sin(v \sin bx) = 2 \sum_0^{\infty} J_{2r+1} \sin \overline{2r+1} bx$$

to evaluate the integrals, where $J_n [= J_n(v)]$ is the Bessel function of the n th order and a dash over the summation sign indicates that the coefficient of J_0 is half that of the others. The real part of the integral is then

$$2 \sum_0^{\infty} J_{2r} \int_{-p/2}^{p/2} \cos ulx \cos 2rbx \, dx - 2 \sum_0^{\infty} J_{2r+1} \int_{-p/2}^{p/2} \sin ulx \sin \overline{2r+1} bx \, dx$$

or

$$\begin{aligned} & \sum_0^{\infty} J_{2r} \int_{-p/2}^{p/2} \{\cos(ul + 2rb)x + \cos(ul - 2rb)x\} dx \\ & + \sum_0^{\infty} J_{2r+1} \int_{-p/2}^{p/2} \{\cos(ul + \overline{2r+1} b)x - \cos(ul - \overline{2r+1} b)x\} dx \end{aligned}$$

Integrating the above, we obtain

$$\begin{aligned} & p \sum_0^{\infty} J_{2r} \left\{ \frac{\sin(ul + 2rb)p/2}{(ul + 2rb)p/2} + \frac{\sin(ul - 2rb)p/2}{(ul - 2rb)p/2} \right\} \\ & + p \sum_0^{\infty} J_{2r+1} \left\{ \frac{\sin(ul + \overline{2r+1} b)p/2}{(ul + \overline{2r+1} b)p/2} - \frac{\sin(ul - \overline{2r+1} b)p/2}{(ul - \overline{2r+1} b)p/2} \right\} \quad \dots (2) \end{aligned}$$

The integral corresponding to the imaginary part of the diffraction integral

is zero. One can see that the magnitude of each individual term of (2) attains its highest maximum (the other maxima being negligibly small compared to the highest) when its denominator vanishes. Also, it can be seen that when any one of the terms is maximum, all the others have negligible values as the numerator of each cannot exceed unity and the denominator is some integral non-vanishing multiple of b which is sufficiently large. So the maxima of the magnitude of (2) correspond to the maxima of the magnitudes of the individual terms. Hence the maxima occur when

$$u \pm nb = 0 \quad n(\text{an integer}) \geq 0 \quad \dots \quad (3)$$

where n is any even or odd positive integer. The equation (3) gives the directions in which the magnitude of the amplitude is maximum which correspond also to the maximum of the intensity. If θ denotes the angle between such a direction in the XZ-plane along which the intensity is maximum and the direction of the incident light, (3) can be written as

$$\sin \theta = \pm \frac{n\lambda}{\lambda^*} \quad \dots \quad (4)$$

remembering that $u = 2\pi/\lambda$ and $b = 2\pi/\lambda^*$. This formula is identical with the formula (1) given in the first section. The magnitudes of the various components in the directions given by (4) can be calculated if we know,

$$J_n \text{ or } J_n(v) \text{ or } J_n(2\pi\mu L/\lambda).$$

Thus the relative intensity of the m th component to the n th component is given by

$$\frac{J_m^2(v)}{J_n^2(v)} \quad \text{where } v = 2\pi\mu L/\lambda.$$

In the undisturbed state of the medium there is no variation of the refractive index, i.e., $\mu = 0$. In this case all the components vanish except the zero component for

$$J_m(0) = 0 \text{ for all } m \neq 0 \text{ and } J_0(0) = 1.$$

In the disturbed state, the relative intensities depend on the quantity v or $2\pi\mu L/\lambda$ where λ is the wave-length of the incident light, μ is the maximum variation of the refractive index and L is the path traversed by light in the medium. We have calculated the relative intensities of the various components which are observable for values of v lying between 0 and 8 at different steps (Fig. 1).

Fig. 1 shows that the number of observable components increases as the value of v increases. When $v = 0$, we have only the central component. As v increases from 0, the first orders begin to appear. As v increases still more, the intensity of the central component decreases steadily and the first orders increase steadily in their intensity till they attain maximum intensity when the zero order will nearly vanish and the second orders will have just appeared. As v increases still more, the zero order is reborn and increases

Diffraction of Light by High Frequency Sound Waves—I 411

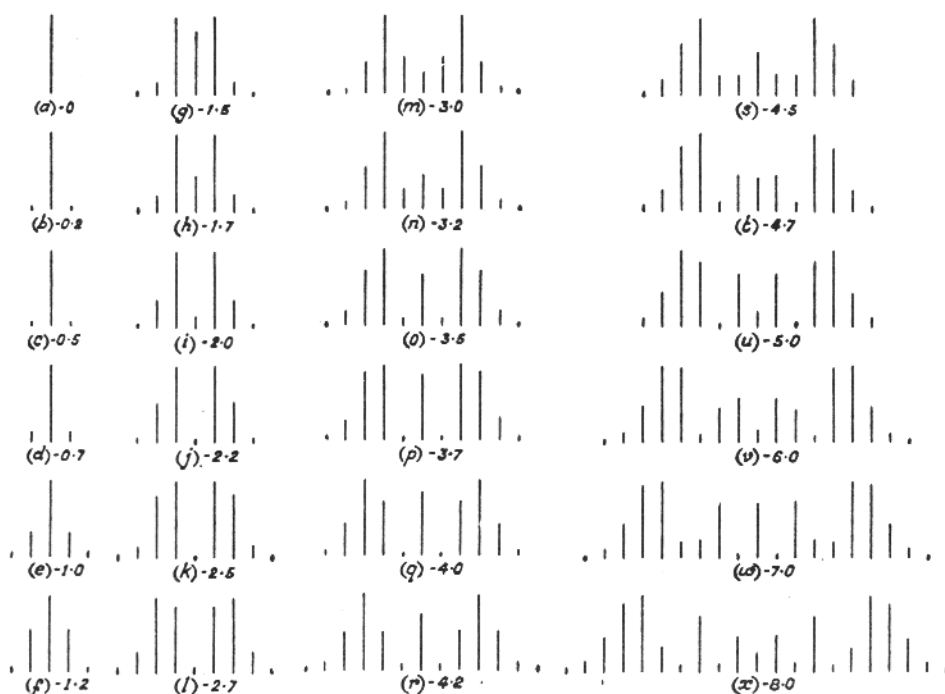


FIG. 1.

Relative intensities of the various components in the diffraction spectra.

(For tables, see Watson's *Bessel Functions and Report of the British Association*, 1915.)

in its intensity, the first orders fall in their intensity giving up their former exalted places to the second orders, while the third orders will have just appeared and so on.

Our theory shows that the intensity relations of the various components depend on the quantity v or $2\pi\mu L/\lambda$. Thus an *increase* of μ (*i.e.*, an increase of the supersonic intensity which creates a greater variation in the refractive index of the medium) or an *increase* of L , or a *decrease* of λ should give similar effects *except* in the last case where the directions of the various beams will be altered in accordance with (4).

3. Interpretation of Bär's Experimental Results.

(a) *Dependence of the effect on the supersonic intensity.*—Bär has observed that only the zero order (strong) and the first orders (faint) are present when the supersonic intensity is not too great. He found that more orders appear as the supersonic intensity is increased but that the intensity of the zero order decreases while the first orders gain in their intensity. Increasing the supersonic intensity more, he found that the first order would become very faint while the second and third orders will have about the same intensity. The figures 1a of his paper may very well be compared

with our figures 1(c), 1(h) and 1(k). Thus, we are able to explain the appearance of more and more components and the wandering of the intensity amongst them as the supersonic intensity is increased, in a satisfactory manner.

(b) *Dependence of the effect on the wave-length of the incident light.*—We have already pointed out that the effects due to an increase of μ caused by an increase of supersonic intensity are similar due to those with a decrease of λ except for the fact that the positions of the components of the emerging light alter in accordance with (4). Bär has obtained two patterns of the phenomenon by using light with wave-lengths 4750\AA and 3650\AA . He obtained, using the former seven components and using the latter eleven components in all. He also observed great variations in the intensities of the components. Not only is the increase in the number of components an immediate consequence of our theory, but we can also find the pattern with 3650\AA if we assume the pattern with 4750\AA . The pattern with the latter in Bär's paper shows a strong resemblance to our figure 1(p) for which $2\pi\mu L/\lambda$ is 3.7. Thus we can calculate $2\pi\mu L/\lambda$ when λ is 3650\AA . It comes to about 4.8. Actually our figure for which $2\pi\mu L/\lambda$ is 4.8 closely corresponds to Bär's pattern with 3650\AA .

(c) *Dependence of the effect on the length of the medium which the light traverses.*—It is clear from our theory that an increase of L corresponds to an increase of v and that the effects due to this variation would be similar to those with an increase of the supersonic intensity. But the basis of our theory does not actually cover any large change in L . However, we should find more components and the wandering of the intensity amongst the various components.

4. Summary.

(a) A theory of the phenomenon of the diffraction of light by sound-waves of high frequency in a medium, discovered by Debye and Sears and Lucas and Biquard, is developed.

(b) The formula

$$\sin \theta = \pm \frac{n\lambda}{\lambda^*} \quad n \text{ (an integer)} \geq 0$$

which gives the directions of the diffracted beams from the direction of the incident beam and where λ and λ^* are the wave-lengths of the incident light and the sound wave in the medium, is established. It has been found that the relative intensity of the m th component to the n th component is given by

$$J_m^2(2\pi\mu L/\lambda) / J_n^2(2\pi\mu L/\lambda)$$

where the functions are the Bessel functions of the m th order and the n th order, μ is the maximum variation of the refractive index and L is the path traversed by light. These theoretical results interpret the experimental results of Bär in a very gratifying manner.

THE DIFFRACTION OF LIGHT BY SOUND WAVES OF HIGH FREQUENCY : PART II.

BY C. V. RAMAN

AND

N. S. NAGENDRA NATH.

(From the Department of Physics, Indian Institute of Science, Bangalore.)

Received October 4, 1935.

1. Introduction.

IN the first¹ of this series of papers, we were concerned with the explanation of the diffraction effects observed when a beam of light traverses a medium filled by sound waves of high frequency. For simplicity, we confined our attention to the case in which a plane beam of light is normally incident on a cell of the medium with rectangular cross-section and travels in a direction strictly perpendicular to the direction along which the sound waves are propagated in the medium. By taking into account the corrugated form of the wave-front on emergence from the cell, the resulting diffraction-effects were evaluated. This treatment will be extended in the present paper to the case in which the light waves travel in a direction inclined at a definite angle to the direction of the propagation of the sound waves. The extension is simple, but it succeeds in a remarkable way in explaining the very striking observations of Debye and Sears² who found a characteristic variation of the intensity of the higher orders of the diffraction spectrum when the angle between the incident beam of light and the plane of the sound waves was gradually altered.

We shall first set out a simple geometrical argument by which the changes in the diffraction phenomenon which occur with increasing obliquity can be inferred from the results already given for the case of the normal incidence. An analytical treatment then follows which confirms the results obtained geometrically.

2. Elementary Geometrical Treatment.

The following diagrams illustrate the manner in which the amplitude of the corrugation in the emerging wave-front alters as the incidence of light on the planes of the sound waves is gradually changed. In the diagrams,

¹ C. V. Raman and N. S. Nagendra Nath, *Proc. Ind. Acad. Sci.*, 1935, 2, 406-412.

² P. Debye and F. W. Sears, *Proc. Nat. Acad. Sci. (Washington)*, 1932, 18, 409.

the planes of maximum and minimum density caused by the sound waves at any instant of time are indicated by thick and thin lines (e.g., AB and CD) respectively. The paths of the light rays are represented by dotted lines in Figs. 1 (b), (c) and (d). As we are mainly interested in the calculation of the phase-changes which the incident wave undergoes before it emerges from the cell, the bending of the light rays within the medium may, in virtue of Fermat's well-known principle, be ignored without a sensible error, *provided* the total depth of the cell is not excessive.

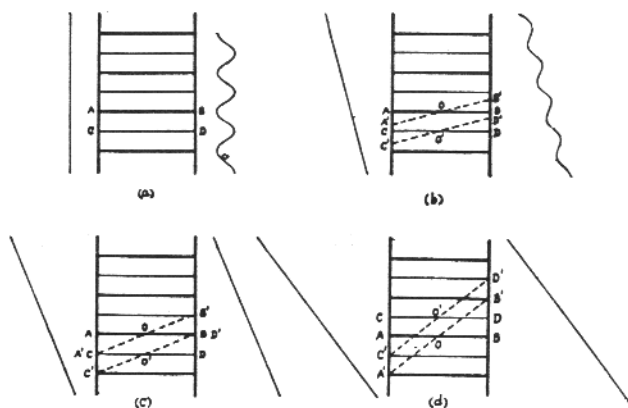


FIG. 1.

Considering the variation in the refractive index to be simply periodic, the neighbouring light-paths with maximum and minimum optical lengths AB and CD respectively, in the case of normal incidence, are shown in Fig. 1(a). The lines AB and CD are separated by $\lambda^*/2$ where λ^* is the wave-length of the sound waves. The difference between the maximum and the minimum optical lengths gives a measure of the corrugation of the wave-front on emergence. Considering now a case in which the light rays make an angle ϕ with the planes of the sound waves, we may denote the maximum and the minimum optical lengths by A'B' and C'D' respectively. These would be symmetrically situated with respect to AB and CD, and would tend to coincide with them as ϕ is decreased. The optical length of A'B' is *less* than that of AB, for the refractive index at any point except at O is less than the constant maximum refractive index along AB, ϕ being small. On the other hand, the optical length of C'D' is *greater* than that of CD, for the refractive index is minimum along CD. A simple consideration of the above shows that the difference between the optical lengths of A'B' and C'D' is less than that between those of AB and CD. As this difference gives twice the amplitude of the corrugation of the emerging wave-front, it follows, in the case shown in Fig. 1 (b), that the amplitude of the

Diffraction of Light by Sound Waves of High Frequency—II 415

corrugation of the emerging wave-front is less than that in the case of Fig. 1 (a).

Fig. 1 (c) illustrates a case when the maximum optical length is just equal to the minimum optical length. This occurs when the direction of the incident beam is inclined to the planes of the sound-wave-fronts at an angle α_1 given by $\tan^{-1} \frac{B'B}{OB} = \tan^{-1} \frac{\lambda^*/2}{L/2} = \tan^{-1} (\lambda^*/L)$. That the optical lengths of A'B' and C'D' in Fig. 1 (c) are equal follows by a very simple geometrical consideration. Thus, when light rays are incident on the sound waves at an angle $\tan^{-1} (\lambda^*/L)$, the amplitude of the corrugation of the emerging wave-front vanishes, *i.e.*, a plane incident beam of light remains so when it emerges from the medium. This result would also be true whenever $\alpha_n = \tan^{-1} (n\lambda^*/L)$, $n \neq 0$. The case when $n=2$ is illustrated in Fig. 1 (d). In all these cases the diffraction effects disappear. As the corrugation vanishes when ϕ is α_{n+1} or α_n , there is an intermediate direction which makes an angle β_n with the sound waves giving the maximum corrugation if light travels along that direction. We can take $\beta_0 (= 0)$ to represent the case when the incident beam of light is parallel to the sound waves.

Thus, we have deduced that the corrugation of the emerging wave-front is maximum when the direction of light is parallel to the sound waves [$\beta_0 (= 0)$], decreases steadily to zero as the inclination ϕ between the incident light and the sound waves is increased to α_1 , increases to a smaller maximum as ϕ increases from α_1 to β_1 , decreases to zero as ϕ increases from β_1 to α_2 , increases to a still smaller maximum as ϕ increases from α_2 to β_2 , and so on.

(I)

As the variation of the refractive index is simply periodic along the direction normal to the sound-wave-fronts, it follows that the optical length of the light path is also simply periodic along the same direction when the incident light rays are parallel to the sound waves. This means that the corrugation of the emerging wave-front is also simply periodic. When the incident light rays are incident at an angle ϕ to the sound waves, the optical length of the light path would be simply periodic in a direction perpendicular to the light rays. This means that the emerging wave-front would be tilted by the angle ϕ about the line of the propagation of the sound waves and that its corrugation would be simply periodic along the same line.

We have shown in our previous paper that a simply periodic corrugated wave is equivalent to a number of waves travelling in directions which make angles, denoted by θ , with the direction of the incident beam given by

$$\sin \theta = \pm \frac{n\lambda}{\lambda^*} \quad n \text{ (an integer)} > 0 \quad \dots (1)$$

where λ is the wave-length of the incident light. In view of the results obtained in the previous paragraph, the formula (1) would also hold good when the incident light is a small angle with the sound waves.

The relative intensities of the various diffraction spectra which depend on the amplitude of the corrugation should obey a law similar to the one in the case of the normal incidence.

Thus, we find that the results in the case of an oblique incidence would be similar to those of the normal incidence with the amplitude of the corrugation modified. Hence, we deduce, in virtue of the statement I, the following results, assuming the results, in the case of normal incidence, obtained in our earlier paper.

The diffraction spectrum will be most prominent when $\phi = 0$. The intensity of the various components wander when ϕ is increased. When ϕ increases from zero to α_1 , the number of the observable orders in practice decreases and when $\phi = \alpha_1$ all the components disappear except the central one which will attain maximum intensity. This does not mean that the intensities of all the orders except the central one decrease to zero monotonically as ϕ varies from zero to α_1 , but some of them may attain maxima and minima in their intensities before they attain the zero intensity when $\phi = \alpha_1$. This is obvious in virtue of the property that the intensity of the n th component depends on the square of the Bessel function J_n . As ϕ increases from α_1 to β_1 the intensity of the central component falls and the other orders are reborn one by one. As ϕ increases from β_1 to α_2 , the number of observable orders decreases and when $\phi = \alpha_2$ all the orders vanish except the central one which will attain the maximum intensity and so on.

3. Analytical Treatment.

In the following, we employ the same notation as in our earlier paper. The optical length of a path in the medium parallel to the direction of the incident light making an angle ϕ with the sound waves may be easily calculated. It is

$$\int_0^{L \sec \phi} \mu(s) ds$$

or

$$\mu_0 L \sec \phi - \mu \int_0^{L \sec \phi} \sin b(x - s \sin \phi) ds.$$

Integrating we obtain the integral as

$$\mu_0 L \sec \phi - \frac{\mu}{b \sin \phi} \{ \sin (bL \tan \phi) \sin bx + [\cos (bL \tan \phi) - 1] \cos bx \}.$$

The last term can be written as

$$-A \sin bx + B \cos bx$$

where

$$A = \frac{\mu}{b \sin \phi} \sin (bL \tan \phi)$$

$$B = -\frac{\mu}{b \sin \phi} [\cos (bL \tan \phi) - 1].$$

Thus the optical length of the path can be written as

$$\mu_0 L \sec \phi - \sqrt{A^2 + B^2} \sin b \left(x - \tan^{-1} \frac{B}{A} \right).$$

Ignoring the constant phase factor, the optical length is

$$\mu_0 L \sec \phi - \frac{2\mu}{b \sin \phi} \sin \left(\frac{bL \tan \phi}{2} \right) \sin bx.$$

If the incident light is

$$\exp \left[2\pi i v \left(t - \frac{x \sin \phi}{c} \right) \right]$$

when it arrives at the face of the cell, it will be

$$\exp \left[\frac{2\pi i}{\lambda} \left(ct - x \sin \phi - \int_0^{L \sec \phi} \mu(s) ds \right) \right]$$

when it arrives at the face from which it emerges.

The amplitude of the corrugated wave at a point on the screen whose join with the origin has its x -direction-cosine l , depends on the evaluation of the diffraction integral

$$\int_{-p/2}^{p/2} \exp \left[\frac{2\pi i}{\lambda} \left\{ (l - \sin \phi)x + \frac{2\mu}{b \sin \phi} \sin \left(\frac{bL \tan \phi}{2} \right) \sin bx \right\} \right] dx.$$

The evaluation of the integral and the discussion of its behaviour with respect to l may be effected in the same way as in our earlier paper. Maxima of the intensity due to the corrugated wave occur in directions making angles, denoted by θ , with the direction of the incident beam when

$$\sin (\theta + \phi) - \sin \phi = \pm \frac{n\lambda}{\lambda_*} \quad n \text{ (an integer)} > 0 \quad \dots (1)$$

The relative intensity of the m th order to the n th order is given by

$$\frac{J_m^2(v)}{J_n^2(v)} \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots (2)$$

where

$$v = \frac{2\pi}{\lambda} \cdot \frac{2\mu}{b \sin \phi} \sin \left(\frac{bL \tan \phi}{2} \right) \\ = \frac{2\pi\mu L}{\lambda} \sec \phi \frac{\sin t}{t} \text{ where } t = \frac{bL \tan \phi}{2} = \frac{\pi L \tan \phi}{\lambda^*}.$$

The expression for the relative intensities in our earlier paper can be obtained from (2) by making $\phi \rightarrow 0$ when $v \rightarrow \frac{2\pi\mu L}{\lambda} = v_0$. So the expression for the relative intensities

$$J_m^2(v_0)/J_n^2(v_0) \quad \dots \quad \dots \quad \dots \quad \dots \quad (3)$$

in the case of normal incidence will change to

$$J_m^2(v)/J_n^2(v)$$

where

$$v = v_0 \sec \phi \frac{\sin t}{t} \quad \dots \quad \dots \quad \dots \quad \dots \quad (4)$$

and

$$t = \frac{\pi L \tan \phi}{\lambda^*}.$$

Even if ϕ be small so that $\sin \phi \approx \tan \phi \approx \phi$, it is *not* justifiable to write $\sin t \approx t$ unless $\pi L \phi / \lambda^*$ is also small to admit the approximation. As $\pi L / \lambda^*$ is sufficiently large we should expect great changes in the diffraction phenomenon even if ϕ be a fraction of a degree. v vanishes when

$$t = n\pi \quad n \text{ (an integer)} > 0,$$

that is, when $L \tan \phi = n\lambda^*$,

or

$$\phi = \tan^{-1} \frac{n\lambda^*}{L}, \quad n \text{ (an integer)} > 0,$$

confirming the same result obtained geometrically. Whenever v vanishes, it can be seen that the amplitude of the corrugation of the wave-front also vanishes. The statement I in Section 2 and the consequences with regard to the behaviour of the intensity among the various orders can all be confirmed by the expression (3).

In the numerical case when $L = 1$ cm., and $\lambda^* = 0.01$ cm., the amplitude of the corrugation vanishes $\tan \alpha_1 = 0.01$ or $\alpha_1 = 0^\circ 34'$. This means that as ϕ varies from 0° to $0^\circ 34'$, the relative intensities of the various orders wander according to (2) till when $\phi = 0^\circ 34'$, all the orders disappear except the central one which attains maximum intensity. This does not mean that the intensities of all the orders except the central one decrease monotonically to zero but they *may possess* several maxima and minima before they become zero. The intensity of the n th order depends on the behaviour

Diffraction of Light by Sound Waves of High Frequency—II 419

of $J_n^2 \left[v_0 \sec \phi \frac{\sin (\pi L \tan \phi / \lambda^*)}{(\pi L \tan \phi / \lambda^*)} \right]$ under the above numerical conditions as ϕ varies from 0° to $0^\circ 34'$. As ϕ just exceeds $0^\circ 34'$, all the orders are reborn one by one till a definite value of ϕ after which they again fall one by one and when $\phi = 1^\circ 8'$, all the orders disappear except the central one.

The numerical example in the above paragraph shows the delicacy of the diffraction phenomenon. If the wave-length is quite small, the diffraction phenomenon will be present in the case of the strictly normal incidence as the relative intensity expression (3) does not depend on λ^* but will soon considerably change even for slight variations of ϕ as the relative intensity expression (4) depends on λ^* . One should be very careful in carrying out the intensity measurements in the case of normal incidence, for even an error of a few minutes of arc in the incidence will affect the intensities of the various orders.

4. Comparison with the experimental results of Debye and Sears.

Debye and Sears make the following statement in their paper: "Fixing the attention on one of the spectra *preferably of higher order*, one can observe that it attains its maximum intensity if the trough is turned through a small angle such that the primary rays are no longer parallel to the planes of the supersonic waves. Different settings are required to obtain highest intensities in different orders. If the trough is turned continuously in one direction, starting from a position which gave the highest intensity to one of the orders, the intensity decreases steadily, goes through zero, increases to a value much smaller than the first maximum, decreases to zero a second time and goes up and down again through a still smaller maximum." This statement very aptly describes the behaviour of the function

$$J_n^2 \left[v_0 \sec \phi \frac{\sin (\pi L \tan \phi / \lambda^*)}{(\pi L \tan \phi / \lambda^*)} \right]$$

as ϕ alters under the conditions imposed in the above statement. The zeroes and the maxima of the intensity of the n th order, as a function of ϕ , correspond to the zeroes and the maxima of the above function.

5. Summary.

The theory of the diffraction of light by sound waves of high frequency developed in our earlier paper is extended to the case when the light beam is incident at an angle to the sound wave-fronts, both from a geometrical point of view and an analytical one. It is found that the maxima of intensity of the diffracted light occur in directions which make definite angles, denoted by θ , with the direction of the incident light given by

$$\sin (\theta + \phi) - \sin \phi = \pm \frac{n\lambda}{\lambda^*}, \quad n \text{ (an integer)} \geq 0$$

where λ and λ^* are the wave-lengths of the incident light and the sound waves in the medium. The relative intensity of the m th order to the n th order is given by

$$J_m^2 \left(v_0 \sec \phi \frac{\sin t}{t} \right) / J_n^2 \left(v_0 \sec \phi \frac{\sin t}{t} \right)$$

where $v_0 = \frac{2\pi\mu L}{\lambda}$, $t = \frac{\pi L \tan \phi}{\lambda^*}$, ϕ is the inclination of the incident beam of light to the sound waves, μ is the maximum variation of the refractive index in the medium when the sound waves are present and $L \sec \phi$ is the distance of the light path in the medium. These results explain the variations of the intensity among the various orders noticed by Debye and Sears for variations of ϕ in a very gratifying manner.

Some important dates in the life of C. V. Raman

November 7, 1888	- Born at Thiruvanaikkaval near Tiruchirapalli
1892-1902	- Early education at Vishakhapatnam
1900	- Matriculation Exam
1902	- F.A. Exam Joins Presidency College, Madras
1904	- B.A., 1st Rank, Gold Medal
1906	- First paper published in <i>Phil. Mag.</i> , London
1907	- M.A.; Financial Civil Service Exam, 1st Rank - Marriage to Loka Sundari - Posted as Assistant Accountant-General, Indian Finance Deptt, Calcutta - Starts working at the Indian Association for the Cultivation of Science (IACS), Calcutta
1907-1917	- Officer, Finance Deptt, at Calcutta, Rangoon, Nagpur, Calcutta
July 1917	- Palit Professor of Physics, Calcutta University
November 1919	- Secretary, IACS
1921	- First visit to England
1924	- Elected Fellow, Royal Society, London
Feb. 28, 1928	- Discovery of Raman Effect at Calcutta
March 16, 1928	- First public lecture on the Raman Effect before the South Indian Science Association at the Central College, Bangalore
1929	- Knighthood of the British Government
1930	- Nobel Prize for Physics - Hughes Medal of the Royal Society
March 31, 1933	- Director, Indian Institute of Science, Bangalore
1934	- Indian Academy of Sciences established
1935-36	- Raman-Nath Theory: Diffraction of light by ultrasonic waves
1937	- Resigns the Directorship of IISc., continues as Professor & Head, Deptt of Physics
1940	- Raman-Nedungadi discovery of the soft mode
1942	- Franklin Medal
July 1948	- Retires from IISc., Raman Research Institute established; appointed National Professor
1954	- Bharat Ratna
1957	- International Lenin Prize of the Soviet Union
1961	- Member, Pontifical Academy of Sciences, The Vatican
November 21, 1970	- Passes away at Bangalore

